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Influence of Various Factors on Stability of CoSPc in LPG Sweetening Process

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Abstract—IFP Group Technology “Sulfrex process” was used in Iran’s South Pars Gas Complex Refineries for removing sulfur compounds such as mercaptans, carbonyl sulfide and hydrogen sulfide, which uses sulfonated cobalt phthalocyanine dispersed in alkaline solution as catalyst. In this technology, catalyst and alkaline solution were used circularly. However the stability of catalyst due to effect of some parameters would reduce with the running of the unit and therefore sweetening efficiency would be decreased. Hence, the aim of this research is study the factors effecting on the stability of catalyst.

***Keywords*—**sulfonated cobalt phthalocyanine, mercaptans, stability, catalyst, sulfur.

I. INTRODUCTION

THE Sulfrex process is based on the ability of a sulfonated cobalt phthalocyanine to catalyze the oxidation of mercaptans to disulfides in alkaline medium. In this work attention is paid to the stability of CoSPc in alkaline solution which can provide some guides for the design of parameters in LPG sweetening process. Already, in this field, similar work has been performed in laboratory scale, but our research has been done in refinery scale with 2000MMCF per day of row feed. Note that all used data in this paper has been extracted from phase 5th refinery of South Pars Gas Complex.

II. SWEETENING PROCESS DESCRIPTION

The mercaptans are extracted by an aqueous solution of caustic soda according to Eq. (1).

$$RSH + NaOH \longleftrightarrow RSNa + H_2O \qquad (1)$$

The process reduces the total sulfur content in the final product and it is suitable for NGL fractions and LPG. Reaction (1) is reversible, and with increasing molecular weight of mercaptans that there is a sharp fall in the conversion into mercaptide. The forward reaction is favored by low temperature, low molecular weight of mercaptans, and high caustic concentration. In mercaptan extraction units, fresh feed is charged to an extraction column in which mercaptans are extracted by a counter current about 12-15 % wt caustic stream.

The treated product passes overhead to storage or downstream processing. The rich caustic solution containing Sulfrex catalyst flows from the bottom of the extraction column to the regenerator section through a steam heater. Air is injected into this stream, and the mixture flows upward through the oxidizer, where caustic is regenerated by conversion of mercaptans to disulfide oils. The oxidizer effluent flows into the disulfide separator, where spent air, caustic-entrained hydrocarbons, disulfide oil, and regenerated caustic solution are separated. The regenerated caustic stream is returned to the extraction column. Successive Sulfrex catalysis system extraction and regeneration steps decrease the concentration of caustic solution due to the following reasons, which in turn lowers the extraction efficiency [1].

1. Purging: To avoid increasing of salt (Na_2CO_3 and Na_2S) in the circulating caustic solution, because they can’t be removed by the regeneration procedure, the caustic circuit must be partially purged. Purging is done from disulfides separator bottom on a frequency before the fresh caustic make up injection.
2. The water generation due to the extraction/oxidation process.
3. The caustic solution loss through the sweetened propane and butane wet stream coming from the extractor’s top.
4. The soda consumption due to the saltification reactions with CO_2 and H_2S. Due to COS, when it is present in the propane feed, hydrolyses to H_2S and CO_2 during extraction. So Hydrogen sulfide and carbon dioxide react with caustic with the following competing reactions:

$$H_2S + 2\,NaOH \longrightarrow Na_2S + 2H_2O \qquad (2)$$

$$CO_2 + 2\,NaOH \longrightarrow Na_2CO_3 + H_2O \qquad (3)$$

Therefore, to restore the right concentration of NaOH, fresh caustic make up are provided.

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III. RESULTS AND DISCUSSION

A. Measurement of the Catalyst Active Agent in Caustic Solution

Sulfonated Cobalt phthalocyanine (CoSPc) with molecular formula, ($C_{32}H_{16}N_8CO(SO_3Na)_n$) used as catalyst in caustic solution. The concentration of catalyst active agent (Co^{2+}) in caustic solution was measured using the ultraviolet spectrophotometer (Model DR2800 Hach) according to the Beer Ɫambert law .In this work we used this law in order to draw the calibration curve adsorption/cobalt concentration in the solution. The calibration curve produced using the standard procedure showed a good linear relationship in the concentration range of 10-20 mg/L with sulphonated cobalt phthalocyanine in demineralized water. Measuring absorbance of standard solution was done in 660 nm.

B. Effect of Caustic Concentration on the Stability of CoSPc

The catalytic activity of cobalt sulfonated phthalocyanine is guaranteed by its good dispersion in alkaline solution and good catalyst dispersion related with suitable caustic concentration. High caustic concentration has an adverse influence on the reaction of mercaptides to disulfides [5]. In order to expression of these bad effects, dispersion of CoSPc in alkaline solution was studied. 200 ml of alkaline solution include CoSPc was sampled in different concentrations of caustic solution (12%wt to 16%wt), respectively. Ultraviolet spectrophotometer used for measuring of cobalt active agent in solutions. The content of Co^{2+} (active component of catalyst) were proportional to its absorption in ultraviolet spectrum.

TABLE I
ADSORPTION OF CO2+ IN DIFFERENT CONCENTRATION OF CAUSTIC

Caustic Cont (wt %)	Absorbency	Co^{2+} Cont(ppm)
12	1.22	701
13	1.07	670
14	0.99	643
15	0.96	605
16	0.93	584

From figure 1, it can be found that the adsorption of Co^{2+} at 660nm decreases with increasing the concentration of caustic; also the solubility of CoSPc would be lower when the alkaline concentration is higher. In general, results show that the catalyst activity of CoSPc in RSNa conversion to RSSR is decreased with the increases of caustic concentration.

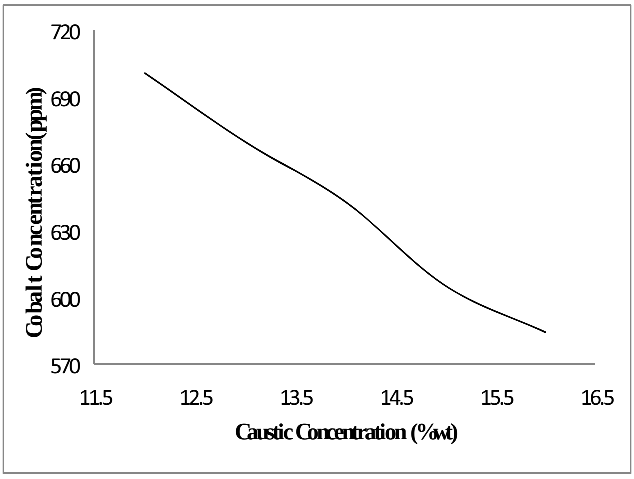

Fig. 1 Relative activity of $Co^{2+}$with caustic concentration

C. Effect of Time and Temperature on the Stability of CoSPc

Experience has shown that caustic regeneration reaction on normal operational process is favored by higher temperature [1]. Therefore temperature in the oxidation reactor (Oxidizer) should be kept at the right value but maximizing of catalyst activity and avoiding its damaging in ranges of circulation time of alkaline solution and temperature should be considered, too. Therefore, in this work finding the optimum range of time and temperature for providing each of mentioned items is intended. To evaluate the effect of these factors on stability of CoSPc, after the changing on process conditions, a series of experiments were tested. The ranges of circulation time were 6 to 12 hour and the ranges of oxidizer temperature were 40 to 55 °C.

TABLE II
RELATIVE ABSORBENCY AND CONCENTRATION OF CO2+ WITH TEMPERATURE AND TIME IN ALKALINE SOLUTION

Circulation Time(hr)	T °C	Absorbency	Co^{2+}Cont (mg/L)
6	40	0.258	163
	45	0.251	157
	50	0.249	149
	55	0.235	136
12	40	0.253	156
	45	0.242	148
	50	0.225	137
	55	0.217	121

The results from the ultra spectrum showed that temperature and time had influence on the quantity of catalyst active component in alkaline solution. From table and figure 2, it could be found that the adsorption of catalyst is decreasing when sulfonated cobalt phthalocyanine was kept in caustic for more than 50 °C and longer time. This means that, the high temperature and long time is cause of low relative quantity of catalyst active component in the solution (Tian et al., 2006. Xia et al., 2008).

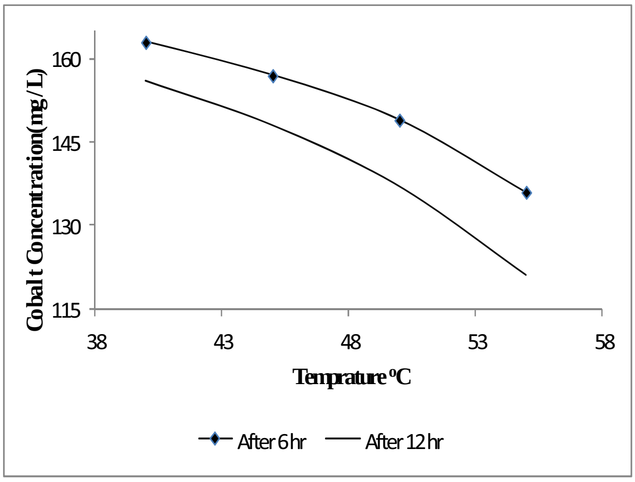

Fig. 2 Relative concentration of $Co^{2+}$with temperature and time

D.Effect of oxygen amount on the Stability of CoSPc

For oxidation of mercaptides the stochiometric requirement of oxygen is 0.25 kg per kg of mercaptan sulfur (Air injection to the oxidizer should be 1.7 Nm^3/h per kg/h of mercaptan sulfur) [1]. However usually it is needed to inject some excess air to the oxidizer to enhance the efficiency of reaction. On the other hand, the color of sulfonated cobalt phthalocyanine changes from green to blue in alkaline solution at ambient temperature. Observations show that the color changing is related to capability of sulfonated cobalt phthalocyanine in oxygen absorbing. For better understanding of the oxygen's role on mercaptides oxidation, reactions and absorbing steps were presented as below:

The main chemical reactions in the Sulfrex process are:

$2RSNa+1/2O_2 + H_2O \rightarrow RSSR + 2NaOH$ (4)

Also, the chemical reactions in detail are:

$RSH \rightarrow RS- + H$ (5)

$NaOH \rightarrow Na + OH-$ (6)

$RS^- + Co^{+2}SPc \rightarrow RS^- \ldots Co^{+2}SPc$

$RS^- \ldots Co^{+2}SPc + O_2 \rightarrow RS^- \ldots Co^{+3}SPc \ldots O_2^-$

$RS^- \ldots Co^{+3}SPc \ldots O_2^- \rightarrow Co^{+2} + RS^o + O_2^-$

Methyl Mercaptan and Ethyl Mercaptan is the main thiols radical of RS^0 *produced from above steps [4].*

Radical transfer:

$CH_3S^o + C_2H^-_5 \rightarrow CH_3S^- + C_2H^o_5$

Dimerization of radicals:

$CH_3S^o + C_2H^o_5 \rightarrow CH_3SSC_2H_5$

$CH_3S^o + CH_3S^o \rightarrow CH_3SSCH_3$

$C_2H^o_5 + C_2H^o_5 \rightarrow C_2H_5SSC_2H_5$

Base regeneration:

$O_2^- + ½ H_2O \rightarrow OH^- + ¾ O_2$

Oxygen is an important reactant in reactions path and has an effect on the stability of CoSPc in alkaline solution. The active component of the catalyst in alkaline solution in presence of more oxygen is unstable [2]. Hence, to determine oxygen content in process, so that stability of catalyst preserved and mercaptide oxidation occurs completely, cobalt concentration as CO^{2+} after changing of oxygen amount in normal operational process, were measured. In this experiments 55, 60, 65, 70 and 75 kg/h was adjusted as an amount of air (required plus excess) during 12hr. Note that in all cases, mercaptide amount entrance to oxidizer nearly, has been constant.

TABLE III
ABSORBENCY/CONCENTRATION of Co^{2+} AT DIFFERENT OXYGEN AMOUNT (T= 45 $^{oC)}$

Rate of Air(kg/hr)	Co2+ Cont (mg/L)
50	211
55	203
60	185
65	146
70	136
75	115

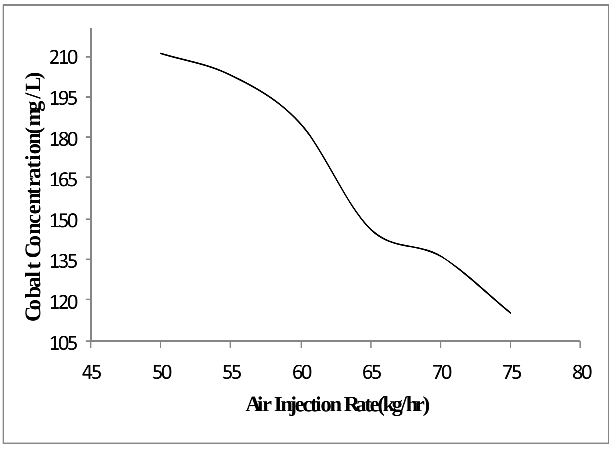

Fig. 3 Relative concentration of cobalt with air rate

The results in Figure 3, express that oxygen has an effect on the stability of CoSPc in alkaline solution, to which it was supposed that oxygen and central cobalt ion in cyclic phthalocyanine could form the binuclear oxygen complex with the formula of ($\ldots CO^{3+} \ldots O^- \ldots O^- \ldots CO^{3+} \ldots$). This dipolymer, when compared with the active mononuclear oxygen complex of $CO^{3+} \ldots O^{2-}_2$, is more stable in the catalysis reaction system [3]. Also laboratory results were shown when air rate was increased (more than needed) and absorbency of Co^{2+} dropped residual mercaptide in alkaline solution and total sulfur of LPG product increased, consequently.

IV. CONCLUSIONS

The solubility of CoSPc would be lower when the caustic concentration is higher. In general, result show that the activity of catalyst (Co^{2+} in CoSPc) is decreased with the increases of caustic concentration. Also, longer circulation time in higher temperature is a negative factor for the stability of sulfonated cobalt phthalocyanine and could lead to the decrease of the concentration of Co^{2+}; on the other hand, excess air and especially amount of oxygen around the catalyst solution have reverse effect on stability of catalyst. The reason for this instability of CoSPc in caustic is that oxygen and CoSPc could form a bi-nuclear oxygen complex. At result, the activity of catalyst was changed evidently by oxygen.

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