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NEW PROCESSES FOR THE TREATMENT OF THE USED ALKALINE SOLUTIONS FROM MEROX AND EXOMER PLANT

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ABSTRACT

In all modern refineries there are the desulphurization installations, used to remove the sulphur compounds from intermediate or finale products of the refineries. These installations generate the used alkaline solutions, relative diluted (5-12%) and significant amounts of organic compounds which include mercaptans and other compounds organic with sulphur, naphthenic acids, crezilic acids, beside a great variety of compounds organic or inorganic. Also it may be present variable amounts of hydrocarbons which constitute a distinct phase.

Present paper presents two new, simple, safe, economically technologies. These processes are integrated for acid consumption reduction. These processes do not use high pressure and/or temperature for treatment.

After treatment, the used solutions together with wastewater are ready to go to the waste water treatment.

The processes were verified at laboratory scale; based on the results obtained in laboratory were build industrial plants for used alkaline treatment. The industrial results confirm the viability of these technologies.

This process is subject of a patent demand (OSIM A/00358/23.04.2010) that received a Gold Medal at International Invention Fair in Middle East, Kuwait City, November 2011.

INTRODUCTION

These processes are applied for treatment and removal of used alkaline solutions from the installations for desulphurization of LPGs, Merox process, (Hydrocarbon Processing, 2006/1) and Gasoline Fractions, Exomer Process, (Hydrocarbon Processing, 2006/2).

In all modern refineries is present the problem of the removal of the alkaline used solutions, relative diluted of the sodium hydroxide (NaOH) or potassium hydroxide (KOH), which result from the desulphurization processes for effluents or products, processes based on alkaline treating. It is evident the desire generated by the corrosive, toxic and pollution potential to process these residues but to not affect the environment.

There are many technological solutions for treating and removal of these residues, mostly are expensive both in terms of investment cost and operating cost, beside are operated at relatively high temperatures and pressures. This paper presents a simple and economic variant for treating these alkaline used solutions. It is perfectly adaptable for the present desulphurization installations from the romanian refineries.

The problem of the used alkaline solutions

The desulphurization processes for removal of the compounds with sulphur being in the intermediate or finale products of the refineries are widely used in modern refineries. These installations generate the alkaline used solutions, relative diluted of sodium hydroxide (NaOH) or potassium hydroxide (KOH). The alkaline used solutions contain between 5 and 12% mass NaOH and significant amounts of organic compounds which are corrosive, toxic or pollutants (sulphur, mercaptides and other organic compounds with sulphur, naphthenic acids as naphthenates, cresylic acids as salts), beside a great variety of organic or inorganic compounds present in amounts more or less significant. Also can be present variable amounts of hydrocarbons which constitute a distinct phase beside the alkaline solution. All of these solutions are considered residues as long as they are not taken by some others industries for processing. It is obvious requirement generated be the corrosive, toxic and pollution potential, to process these residues, but in a manner that does not affect the environment.

The refineries and petrochemical plants (for some time but more acute in the recent years) must face a severe control of all liquid and gaseous effluents, which can cause the air and water pollution. Refinery industry has a historic experience on the utilization of alkaline solutions for the treating of acids contaminants present on the products (hydrogen sulphide, mercaptans and organic acids). Even now alkaline solutions represents the primary agents for this processing because are certain, economic and efficient, and acceptable from point of view of the environment protection. The properly treatment of these solutions is not representing a danger for the environment. A solution adopted by the most refineries in SUA and other countries is to deliver they to an another chemical units. This solution, as long as it's treated by those beneficiaries, is not representing an object of the environment regulations (Suarez, 1996).

The worries regarding these alkaline used solutions are generated by:

- most of the operators are not in cause of the conscience regarding the processing and the reuse of these used solutions;
- improper process design for treating of the used solutions can cause problems in operating;
- used solutions can became danger residues accountable to the environment;
- ungrounded worries regarding the characterization of the alkaline solutions as hazardous residues by the EPA and regarding the removal costs (3USD/gal).

The reason that treatment with hydroxides solutions is used and at this present it is low cost versus hydrotreating (investment costs of 10 - 12.5 times smaller and operating costs of 5 – 22 times smaller). We have to mention that the hydroxides solutions don't represent an answer for all the petroleum fractions from refineries, especially for heavy one.

The table 1 presents a comparison between the processing costs for the two solutions in case of the oil reactor.

Table 1. Comparative costs of the investment and operating for the treating of oil reactor – jet fuel (10000 bpsd).

	Treating with hydroxides	Hydro treating
Investment cost, US $/bbl	150 … 200	1500 … 2500
Operating cost, US $/bbl		
- catalysts and chemicals	0.0172	0.380
- utilities	0.0005	0.025
- staff	0.0060	0.012
Total	0.0237	0.417

At present moment refinery gases, liquefied refinery gases and light gasoline contain H_2S, RSH and COS or cresylic acids who are easily absorbed or extracted with alkaline solutions [Gary, 2001; Kohl, 1997; Strătulă, 1984; Meyers, 2003, Bradley; 1992, Suciu, 1983; Profile, 1995; Hydrocarbon Processing, 2006). Between the existent treatment processes we can mention: (1) the MEROX process for the treating gases and liquefied gases (Hydrocarbon Processing, 2006/1) and the treating with EXOMER solution for catalytic cracking gasoline (Hydrocarbon Processing, 2006/2).

The advantages of the alkaline treating are:

- economy: related with the increased of NaOH cost which was always below the inflation rate [3];
- safety: the control of the alkaline solutions, although aggressive, is easy than many other chemicals;
- effectiveness and controllability: the solutions are effective, easy to prepare, with corresponding pumping and control of the flow rate. Also, the solutions aren't soluble in hydrocarbons, this allows an easy separation of the two phases which have different densities;
- the alkaline used solutions management is simplified by the decision of several companies to treat and to properly remove the used solutions in damage of their reuse.

It is extremely important that every technological process and then the elimination process of the residues to be properly evaluated. So:

- the errors made in the design process lead to increased costs and environment risks;

- mixing more types of alkaline used solutions is not a good solution;

- improper design of the storage tanks (most often undersized);

- treating more types of the used solutions in one installation, often designed only for treating a single type;

- inadequate control of pH at neutralization.

There are many alternatives solutions for treating to remove these used solutions. The typical composition for alkaline used solution from the treating of liquefied gases is presented in the table 2.

The components with a high pollution potential are: sulphide and sodium mercaptide. These determined a high chemical and biological oxygen consumption (COD and BOD) causing problems in the wastewater treatment stations and produce dangerous and smell gases at neutralization.

Table 2. Characteristics of typical used soda solutions.

NaOH free, % mass	2 … 10 (sometimes even more)
Na_2S, NaHS as S, % mass	0.5 … 4
Mercaptide as S, % mass	0.1 … 4
Carbonates as CO_3, % mass	0 … 4
pH	13 … 14

Na total, %	4 … 10
Ammonium	traces

Cresylic solutions from the treating of the catalytic cracking gasoline [2] come generally from two processes:

- extraction and oxidation with strong alkaline solutions;
- oxidation with weak alkaline solutions.

The used solutions from the first case are sold at fair and attractive prices, which often cover the transport costs. These solutions contain at least 10% mass (often until 15%) phenol compounds respective cresols. By treating is recovered the valuable phenol compounds. In the second case the content of phenol compounds is under 5% mass, this it makes unfit for their recovery. Phenol compounds must be carefully removed having regard to the specifications from the entry on treating biological stage of the waste water.

In the table 3 are presented the typical composition for the two types of cresylic solutions.

Table 3. The characteristics of typical cresylic solutions.

	Strong alkaline solutions	Dilute alkaline solutions
NaOH (at pH 7), % mass	10 ... 15	1 … 4
H_2S as S, % mass	0 ... 1	0 ... 0.2
Mercaptide as S, % mass	0 ... 4	0 ... 0.5
Cresylic acids, % mass	10 ... 25	2 ... 5
Carbonates as $C0_3$, % mass	0 ... 0.5	0 ... 0.1
pH	12 ... 14	12 ... 14

Presentation of existing treating solutions at world level

It is clear that we can not try to give our own solution to this problem without see which is the current stage for solving this problem. At this time are many solutions and solving variants for this problem (UOP, 2007; Gondolfe, 1997; Carlos, 2000; US Patent, 1975, 1976, 1980, 1994, 1997/1, 1997/2, 2007; Hydrocarbon Processing, 2006). Many of them are patents are the property of some companies; it is clear that the adoption of such solutions is costly and often can not be supported by users.

In general, existing solutions may qualify so:

- wet partial oxidation of the sodium sulphide at sodium thiosulphate ;
- wet total oxidation of the sodium sulphide at sodium thiosulphate ;
- deep neutralization up to reduced pH for the elimination of H_2S and mercaptans;
- incineration;
- chemical oxidation;
- reuse in other areas of the factory, for example at gasoline treating; in this case result a soda with a high value because the increase content of creslic acids;
- use at DA installation or at the striping acid-waters;
- sending the solutions outside either for treatment or for to use by some other producers from chemical industry domain.

THE EXPERIMENTS CONCERNING USED ALKALINE SOLUTIONS

For all experiments concerning used alkaline solutions we used the analyses methods presented in table 4.

Table 4. The analyse methods for used alkaline soda and waste water.

Analyse	UOM	Methods
USED SODA		
Total alkalinity	% w	UOP 210-76T
Strong base	% w	UOP 210-76T
Weak base	% w	UOP 210-67T
Sodium sulphide	% w	SR 7510-97
Sodium thiosulfate	% w	UOP 423-55
Phenol	mg/l	SR ISO 6439-01
Ammonium	mg/l	SR ISO 5664-01
WASTEWATER		
pH		SR ISO 10523-97
Sulphide	mg/l	SR 7510-97
Solid suspension	mg/l	STAS 6953-81
Extractable in ether	mg/l	SR 7587-96
CCOCr	mg/l	SR ISO 6060-96
Phenol	mg/l	SR ISO 6439-01
Detergents	mg/l	-
Ammonium	mg/l	SR ISO 5664-01 SR ISO 7151-1/01

The complete analyses of used alkaline solutions to be treated (from Romanian refinery) are given in table 5.

Table 5. Analyses of the used alkaline soda

samples before treatment.

No.	Total alkalinity, % w	Strong base, % w	Weak base, % of total alkalinity	Sodium sulphide, % w
1	4.21	3.24	23.04	2.18
2	4.16	3.16	24.04	2.92
3	4.01	3.20	20.20	5.76
4	7.19	6.17	14.18	2.16
5	5.28	4.72	10.61	2.16
6	9.83	8.92	9.26	1.47
7	4.60	4.05	11.96	3.61
8	14.82	12.55	15.32	2.31
9	18.26	12.58	17.56	2.57

No.	Thiosulphate $S_2O_3^{2-}$, % w	Density, d_4^{15}	Phenol, mg/l	Ammonium, mg/l
1	12.3	1.039	376	348
2	12.4	1.033	1242	1290
3	12.2	1.040	1935	1482
4	8.4	1.055	876	908
5	7.2	1.062	1804	225
6	3.6	1.123	3470	164
7	12.6	1.042	62	324
8	13.5	1.173	1275	1154
9	14.2	1.189	1563	979
10	EXOMER - KOH=12.18% w; KOR = 8.65% w			

The treatment of the used alkaline solutions from MEROX process

The new process has next steps:

- dilution with waste water;
- neutralization;
- oxidation.

Every step was experimented in lab and at industrial scale.

In the table 6 are presented the results of the dilution. It is easy to see, after dilution, that every pollutants has (except pH) values under maxim allowable values. In order to reduce pH value the used soda solutions were neutralised with sulphuric acid. In the figure 1 are presented the neutralisation curve for one sample (100 ml sample, sulphuric acid 10% solutions).

Table 6. The analyses of the alkaline use soda (MEROX) after dilution.

Analyse	Sample Lab1	Sample Lab 2	Waste water after treatment	Maxim allowable values
Laboratory				
pH	10.3	9.4	6.6	6.5-8.5
Sulphide total, mg/l	0	0	0	40
Solid suspension, mg/l	47.3	55.2	40.5	150
Extractable in ether, mg/l	15.3	13.2	8.5	4000
CCOCr, mg/l	155.7	97.3	144.0	994
Phenol, mg/l	0.1	0.1	0.1	15
Ammonium, mg/l	0.1	0.1	0.2	12
Industrial				
pH	10.6	9.1	6.6	8.5
Sulphide total, mg/l	0	0	0	40
Solid suspension, mg/l	45.2	52.7	40.5	150
Extractable in ether, mg/l	13.1	15.3	8.5	4000
CCOCr, mg/l	149.2	98.9	144.0	994
Phenol, mg/l	0.1	0.1	0.1	15
Ammonium, mg/l	0.1	0.1	0.2	12

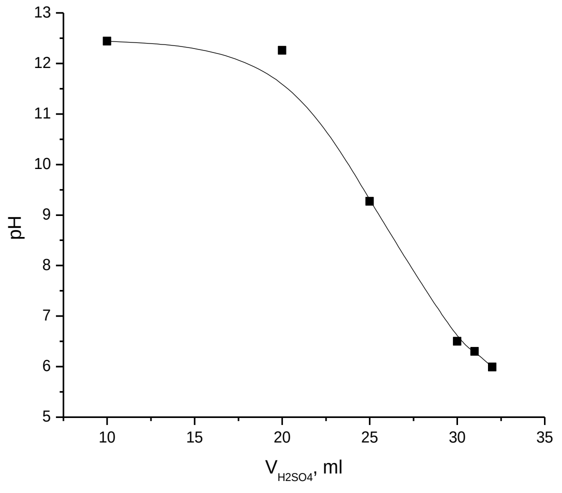

Fig. 1. Neutralization curve for sample 2 (used alkaline solution from MEROX).

One, the most, important observation: under pH 8 we observed an important emission of H_2S. For this reason we limit neutralization till pH 8.5. In this condition, H_2S remain in solution and, in 20-30 minutes is oxidized to sulphur.

The treatment of the used alkaline solutions from EXOMER process

Concerning EXOMER used alkaline solution, the neutralization are presented in figure 2.

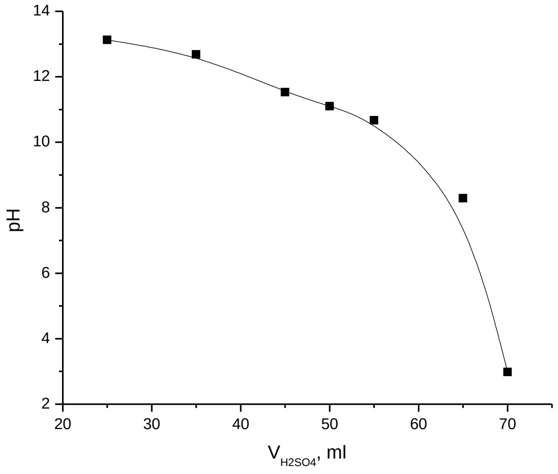

Fig. 2. Neutralization curve for sample 2 (used alkaline solution from EXOMER).

Observations concerning neutralization of used alkaline solutions from EXOMER:

- no H_2S emissions are observed;
- during neutralization appeared two phases: one, organic phase, naphthenic acids, and another, water phase;
- at pH under 2.5-3 all naphthenic acids are separated;
- organic phase can be sent in crude oil if there are not facilities for naphthenic acids treatment;
- water phase with low pH can be used for neutralization of MEROX used alkaline solutions;
- using water phase to neutralize used alkaline solutions from MEROX will reduce acid consumption.

INDUSTRIAL TREATMENT OF THE USED ALKALINE SOLUTIONS FROM MEROX AND EXOMER PROCESSES

Based on these lab experiments we elaborated new processes for the treatment of both used alkaline solutions (MEROX and EXOMER). The both processes are connected, water phase (strong acid) from EXOMER used alkaline solutions treatment are used for neutralization of MEROX used alkaline solutions.

The block diagrams of both processes are presented in figure 3 and 4.

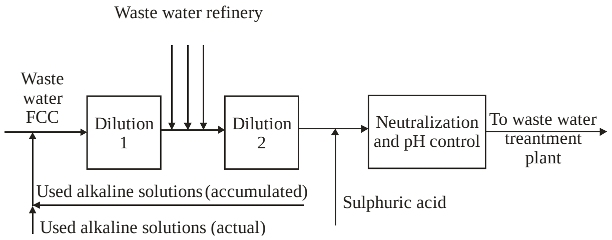

Fig. 3. Block diagram of treatment of MEROX used alkaline solutions.

During industrial testing we change the point of sulphuric acid input from entrance of waste water treatment plant before the chemical stage (clotting basin).

In the table 5 and 6 are presented the results of industrial scale experiments.

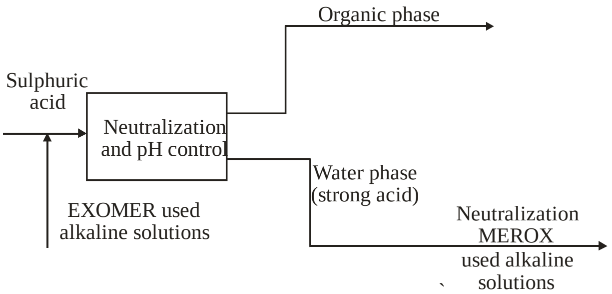

Fig. 4. Block diagram of treatment of EXOMER used alkaline solutions.

The advantages of this process are:

- the proposed technology was proved at laboratory scale;
- all effluents were analyzed according maximum allowable levels;
- the values of the concentration of contaminants in resulted streams are below the limits allowed by maximum allowable levels;
- in the process doesn’t result any gaseous or solid streams with pollution potential;
- the technology ensure that the contaminants remain in the aqueous phase under maximum allowable levels to entry in the water treatment station;
- from this technology does not result new or unknown compounds who can charge water treatment station;
- the technology do not appeal to processes that take place at high temperatures and pressures, does not consume energy in pumping out power to the determination of dilution and neutralization
- the technology does not require use of a highly qualified personnel;
- the technology is simple, safe, easy to control, operating costs are reduced;

- the technology is safe in operation, any trouble shootings can not cause pollution of the environment;
- the technology ensure both current and accumulated alkaline solutions discharge;
- the removal is done within a reasonable time so that in 2012 they will be completely eliminated;
- after 2012 elimination of current soda is at a cadence that can not allow their accumulation;
- from this technology does not result any hazardous wastes;
- the technology provides the reuse of the acid solution from the EXOMER plant to neutralize waste alkaline solutions from MEROX.

This combined process is the object of a Romanian Patent demand (Oprea, 2010).

In the table 7 are presented the results obtained in industrial experiment for the treatment of the used alkaline solutions from MEROX and EXOMER plants.

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Tab. 7. The results of the industrial scale experiments for MEROX and EXOMER used alkaline solutions treatment.

	pH	Total Base Strong base	Sulphide	Phenol	Ammonium	CCOCr	CBO$_5$	Solid suspen-sions	Extractable in ether
		%	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Maxim value allowance at entrance of the waste water treatment plant	6.5-8.5		40	15	12	994		150	4000
Waste water at input	8.6	0.007 0.004	0.92	9,8	11.5	722,8	237,1	264	736
Waste water at input	9.28	0.018 0.006	5,8	10,2	9,2	912	324,6	192	2372
Waste water at input	9.1	0.0173 0.006	8,4	10,4	10,4	890,8	290,4	189	1821
Waste water at input	9.47	0.018 0.009	9,2	10,9	18,2	520,8	201,5	195	1598
Waste water at input	9.3	0.0185 0.007	9.3	11.5	16.2	977	390,4	205	2134
Waste water at input	9.28	0.018 0.006	5,8	10,2	9,2	912	324,6	192	2372
Waste water at input	9.47	0.018 0.009	9,2	10,9	18,2	520,8	201,5	195	1598
Waste water at input	9.3	0.0185 0.007	9.3	11.5	16.2	977	390,4	205	2134
Waste water clotting basin	7.34	0.0076 0.0012	4,9	6,7	7,9	260,2	89,5	36,5	21,4
Waste water clotting basin	7.11	0.0122 0.0013	4.9	6.2	8.76	532	144	87.44	28.6
Waste water clotting basin	8.5	0.0135 0.0019	4.2	9.2	9.32	476	168	92.5	33.9
Waste water clotting basin	8.5	0.010 0.003	4,8	6,5	15,5	516	184,2	52,6	60,7
Waste water clotting basin	8.5	0.0095 0.0048	4,6	5,2	19,8	512	181	84,1	18,4
Waste water clotting basin	8.5	0.0125 0.0016	3,8	6,2	24,5	348,2	157,0	41,5	25,6
Waste water clotting basin	8.11	0.0122 0.0013	4.9	6.2	8.76	532	144	87.44	28.6