

Experimental Studies Concerning Treatment of the Spent Caustic Solutions from Refineries MEROX and EXOMER Units

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The paper presents laboratory and industrial tests on treatment of the spent caustic solutions from refineries MEROX and EXOMER units. We proposed a simple, reliable, safe, easy to control and with low cost. Both types of spent caustic solutions (from MEROX and EXOMER units) are treated together in order to obtain low operation cost. The stream resulted from these treatments are harmless for wastewater treatment unit and do not affect the quality of the wastewater at the entrance in the wastewater unit and of the purified water from this unit.

Keywords: spent caustic, MEROX, EXOMER, hydrogen sulphide, mercaptans, cresols, environmental protection

Based on the study of literature [1] and of the analysis of spent caustic solutions, from the MEROX unit, on the calculations and based on laboratory and industrial discontinuous experiments, presented in [2], authors have synthesized a conception and a new technology for the treatment of these solutions. In essence, the proposal consists in neutralization of mixture wastewater-caustic solutions up to pH of 8.5 asked for the maximum allowable at input of the wastewater treatment unit. This proposal is based on the avoiding of the toxic and smell gas released and on the small value of CCOCr of the mixture, value which is framed between the values provided by analytical control program, and as such does not charge supplementary the wastewater treatment unit. Values of other constituents from the mixture residual water-used caustic solution are also situated under the maximum allowable at input of the wastewater treatment unit, as it was seen from the laboratory and industrial experiments, which direct only dilution. In the experiments made in the laboratory was used purified water for the reasons set in [2].

For neutralization, it was proposed the use of a solution of 10% H₂SO₄, choice motivated by economical considerations and controllability of dosage realized at industrial scale.

Laboratory experiments regarding neutralization of the spent caustic solutions from MEROX unit

Laboratory study had the following steps:

-plotting curves of neutralization of spent caustic solution, curves which were obtained through titration of the caustic solution with a solution of H₂SO₄ 10%, accompanying with the pH measuring of the resulting solution;

-plotting curves of neutralization of mixtures water-used soda, curves obtained through titration of a mixture spent caustic solution – purified water (with dilution 0,2% volume soda over purified water) with a solution of H₂SO₄ 10% w., accompanying with the pH measuring of the resulting solution up to a pH value which is equal to pH of purified water;

-analysis of mixtures obtained, mixtures that simulate at laboratory scale the mixture that is to be achieved at industrial level.

First step of the study tried to discern the neutralization mechanism of used soda and of related phenomena. It were neutralized all samples from the refinery. Experiment consist in using of a quantity of 50 mL spent caustic solution in a beaker with magnetic stirrer, at ambient temperature, and in adding of sulphuric acid 10% wt. with a burette. The pH of resulting solution was permanently measured.

Observation made during the experiments:

-at the beginning of the titration the pH varies slightly;
-at pH values less than 12 the titration curve have a high slope, followed than by a flattening for pH values less than 6;

-there was observed a strong release of hydrogen sulphide and mercaptans at pH values less than 8; this was the reason for what, in some cases, the titration was not performed on up to pH values in acid domain;

-the solutions obtained after neutralization contain sulphur suspensions, meaning that hydrogen sulphide was oxidized due to strong stirring.

In figure 1 is presented only one of the obtained neutralization curves, the other curves being similar, and differences consisting only in the quantity of sulphuric acid utilized for neutralization.

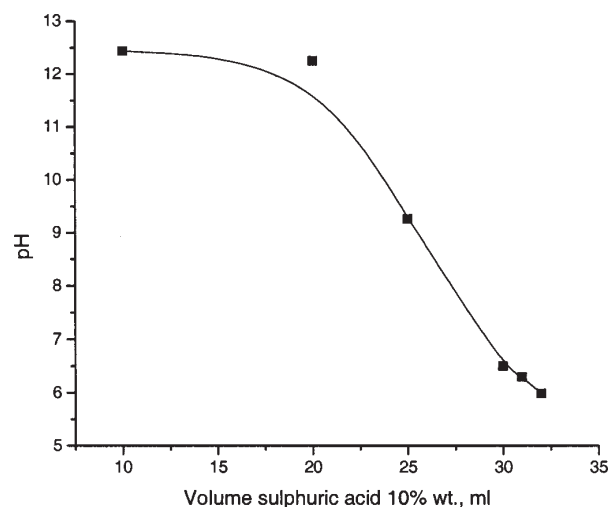


Fig. 1. Neutralization curve for used soda 1

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Even if our decision was to not neutralize first the soda, the experiments above were useful for many reasons:

- it can be evaluated the required quantity of acid for used soda neutralization, quantity depending on the pH value;

- also, the required acid quantity depends on pH value of the water used in dilution;

- neutralization up to pH values less than 8.5 leads releases major quantities of hydrogen sulphide and mercaptans, which it is unacceptable in principle, because the pollution is moved from water in atmosphere;

- the neutralization reaction is exothermal;

- the experiment, applied at the industrial level, that confirms the laboratory ex experiments, has motivated us to use another neutralization alternative.

Having in mind these above, we decided that neutralization of basic compounds from spent caustic solution must be made after previous dilution of soda. Reasons are two:

- the first is related to the possible difficulties on direct neutralization;

- the second is referring to eliminating possibilities of forming of some zones with high local acid concentration, which would cause, in that zone, a strong neutralization reaction. These zones can arrive quickly to acid pH and in this way hydrogen sulphide and mercaptans are releasing, even in the rest of solution pH has high values. This situation is unacceptable due to effects that can appear, namely hydrogen sulphide and mercaptans releasing. Reason of utilization of treated water was explained in [2].

During neutralization of a diluted solution, which means that the concentration of basic compounds is low, with adding of the acid (not so strong) neutralization reaction will perform with reduced rate. In this way is avoiding appearance of neutralized zones with acid pH, hydrogen sulphide and mercaptans releasing being excluded. This way, S²⁻ ion and mercaptans stay in solution, avoiding the air pollution. In laboratory experiments from this section was not observed hydrogen sulphide releasing or sulphur formation that means that adopted solution is adequate to aim of avoiding of hydrogen sulphide formation.

This is an advantage of this solution because neutralization up to acid pH values (less than 4, like is reminded in literature [1]) would require neutralization accomplishment in pressure vessels for hydrogen sulphide and mercaptans capture to avoid air pollution. Captured

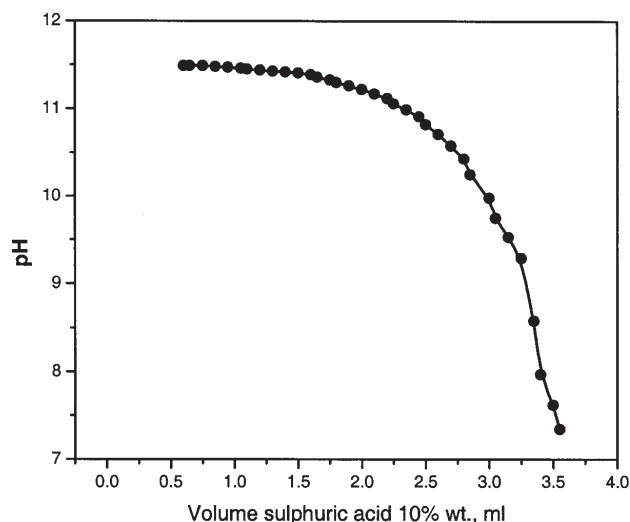


Fig. 2. Neutralization curve for mixture treated water - used soda

gases must be processed in gas desulphurization installation. This solution supposes additional expenses that would charge spent caustic solution disposal cost.

Similar with these presented above there were plotted neutralization curves for formed mixtures from treated water and spent caustic solution. We utilized used soda from storage tanks and both current soda. Neutralization curve is presented in figure 2.

The mixtures obtained based on data from neutralization curves (neutralization performed up to 8.5 pH maximum value) were analyzed. Analysis values of resulted waste waters are presented in table 1.

Data presented in table 1 show that for all pollutants present in wastewater obtained through dilution and neutralization all concentrations are situated under maximum allowable values at input in wastewater treatment unit. In this way, proposed solution is validated by laboratory experiments accomplished with samples taken from industry.

Experiment at industrial scale in discontinuous regime for spent caustic solutions from MEROX unit

Before starting a continuous industrial experiment, in order to check the results obtained in laboratory a test on the industrial installation was made. The experiment in discontinuous regime consists in the reconstitution of the laboratory experiment (table 1).

Table 1
ANALYSIS OF NEUTRALIZED MIXTURES CAUSTIC SOLUTION - TREATED WATER (OBTAINED IN LABORATORY)

Analysis	Treated water	Sample 30 Current soda 1 + treated water	Sample 31 Current soda 2 + treated water	Sample 32 Soda V 2/1 + treated water	Sample 33 Soda V 2/2 + treated water	Sample 34 Soda V 3/1 + treated water	Sample 35 Soda V 3/2 + treated water	Sample 36 Soda V 6/2 + treated water	Maximum allowable values according PCA
pH	6.6	8.6	8.4	8.3	8.1	8.4	8.6	8.5	6.5-8.5
Total sulphides, mg/l	0	0	0	0.01	0.01	0	0	0	40
Solid suspension, mg/l	40.5	43.6	45.2	34.6	48.7	31.6	29.2	37.2	150
Extractible, mg/l	8.5	8.3	16.8	8.2	19.2	9.2	11.4	14.0	4000
CCOCr, mg/l	144.0	168	254.7	168	254	115.2	115	126.7	994
Phenols, mg/l	0.1	0.8	0.26	0.15	1.1	0.9	1.3	0.9	15
Ammonium, mg/l	0.2	0.1	0.15	0.32	0.24	0.07	0.06	0.06	12

Table 2
EXPERIMENTAL RESULTS PERFORMED AT INDUSTRIAL SCALE IN DISCONTINUOUS REGIME

Analysis	Blank	Sample 1	Blank	Sample 2	Maximum allowable values
	Assay 1	Current caustic solution 1	Assay 2	Current caustic solution 2	
pH	10.6	8.3	9.1	8.1	6.5-8.5
Total sulphides, mg/l	0	0	0	0	40
Solid suspension, mg/l	45.2	49.1	52.7	56.2	150
Extractible, mg/l	13.1	11.5	15.3	17.3	4000
CCOCr, mg/l	149.2	182	98.9	289	994
Phenols, mg/l	0.1	0.91	0.1	0.27	15
Ammonium, mg/l	0.1	0.12	0.1	0.17	12

There were utilized the current caustic solutions 1 and 2 [1] diluted in proportion of 100 L caustic solution - 50 m³ treated water. Neutralization was done with 9.5 L of sulphuric acid 98% for current caustic solution 1, respectively with 9 L acid sulphuric 98% for current caustic solution 2.

The results of the experiments after the analysis of taken samples are presented in table 2. It was performed in parallel similar mixtures but without neutralization (watch blank assays from table 2).

Data presented in table 2 show a good concordance with the results obtained in laboratory. We make the same notice concerning the absence of the sulphides explained by the fact that both in laboratory and in the industrial installation had happen an oxidation up to superior valence of sulphur. The results of the industrial test, corroborate with results obtained in the laboratory, confirm the validity of the proposed technology for the treatment of spent caustic solutions from MEROX unit.

Laboratory experiments concerning the removal of the spent caustic solutions from Exomer unit

Based on results of the dilution and neutralization tests of the spent caustic solutions from MEROX unit and the data from literature, we have been preoccupied by the investigation of the possibility of the caustic solutions recovery from Exomer unit.

In figure 3 is presented the neutralization curve of a solution obtained through neutralization of 50 cm³ of spent caustic solution with sulphuric acid 10%.

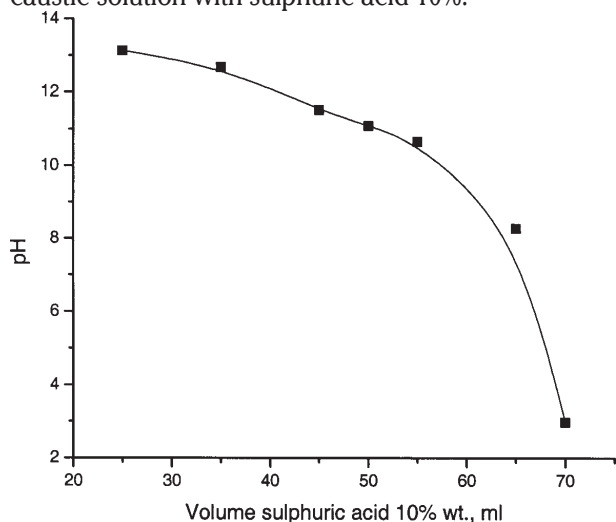


Fig. 3. Neutralization curve for spent caustic solution from EXOMER unit

During neutralization we did the following observations:

- the curve is a typical neutralization curve base-acid;
- during neutralization it was not observed hydrogen sulphide or mercaptans releasing;

- once with the first acid quantities feed into samples, it was observed separation of two phases in the same time with change of the color;

- stopping of stirring it could observe that, after a while, two stages are separated;

- the separation time decreases with decreasing of pH;

- with pH decreasing, quantity of organic phase increase;

- increasing of the volume of the organic phase stopped when pH value was 2.5; at this moment time of sedimentation is minimum, having a reasonable duration, (approximate 3 min);

- for pH=9.6 was taken a sample from aqueous phase (sample 1), when organic phase proportion was about 5% volume;

- for pH=2.95 was taken a sample from aqueous phase (sample 2), when organic phase proportion was about 15% volume.

In table 3 are presented values of analysis of the two samples. Even the CCOCr value for sample 2 exceeds maximum allowable value, that is not a reason of fear, having in mind that neutralization was realized without diluting of the sample.

The removal process of used soda from Exomer unit consists in:

- neutralization (realized continuous or by stages) up to a 2.5 pH value;

- separation of two phases; organic phase formed from cresylic acids represent about 15% from used soda volume;

- utilization of organic (phase cresylic acids) like admixture in crude oil processed; dilution will be extremely reduced, respectively 100 tones cresylic acids (what means 12.5 kg per hour) for 2.7 millions tones crude oil (in which case is desired removal of soda within an year) that represent 37 ppm;

- utilization of resulted solution, strong acid, for neutralization of used soda from MEROX unit; this way the water phase, strong acid, are eliminated; in the same time is produced a massive dilution, eventually remained cresylic acids are eliminated without charging the water treatment station;

- the last but not the least it can make saving of costs for acid for treatment of used soda from MEROX unit according to the presented technology.

The conclusions concerning the validity of the technology proposed after laboratory and industrial experiments in discontinuous regime:

Table 3
RESULTS OF THE EXPERIMENT PERFORMED FOR SODA RESULTED FROM EXOMER UNIT

Analysis	Sample1 pH = 9.6	Sample2 pH = 2.95	Maximum allowable values according PCA
pH	9.6	2.95	6.5-8.5
Total sulphides, mg/l	0	0	40
Solid suspension, mg/l	101.2	50.4	150
Extractible, mg/l	-	-	4000
CCO ₂ Cr, mg/l	32748	5236	994
Phenols, mg/l	-	-	15
Ammonium, mg/l	0.12	0.17	12

- the technology proposed was verified at laboratory scale;

- all the effluents were analyzed according to legal regulations;

- pollutants concentration values in the streams after the treatment of the spent caustic solutions are situated under the allowable limits at input in the wastewater treatment unit; these contributions at the pollutants concentration in the waste water are so small, that they do not cause the exceed of the maximum allowable values, even they are superimposed under the normally existing ones in the waste water;

- in process do not result gaseous or solid flows with pollutant potential;

- the technology ensures that the pollutants remain in aqueous phase, under the maximum allowable levels at the incoming in the wastewater treatment unit;

- from the process do not result new or unknown compounds which can load the wastewater treatment unit;

- the technology does not appeal to other processes at high temperatures and pressures, does not involve important energy consumptions, outside the energy consumed for pumping at the dosing and neutralization;

- the technology does not require the use of a highly qualified staff;

- the technology is simple, safe, easy to control; operating costs are reduced;

- the technology is safe in operation; eventually damages can not cause environment pollution;

- the technology ensures the removal both of accumulated and current caustic solutions;

- the removal of caustic solutions accumulated is done in a reasonable time;

- after that time, removal of current caustic solutions is done at a rate that no longer allows their accumulation;

- in this technology does not result any hazardous waste;
- the technology ensures the recovery of acid aqueous solution resulted from neutralization of spent caustic solution from Exomer unit.

Proposal of a suitable technical solution in terms of environmental requirements and cost of treatment

Based on the experiments achieved in laboratory and in the industrial unit operated discontinuously it was crystallized a concept about how to treat waste caustic solutions. We mention that the technology fully respect the laboratory and industrial experiments and as such, the concentration values of pollutants at the output are strictly in accordance with maximum allowable values at the incoming of wastewater treatment unit.

The industrial unit for the treatment and disposal of spent caustic solutions consists of four integrated modules that treat and simultaneously remove two types of caustic solutions.

- module 1 (fig. 4) represents the unit for dilution and pumping of the spent caustic solutions from MEROX unit;

- module 2 (fig. 5) represents the unit for neutralization of spent caustic solutions from EXOMER unit and for decanting phases obtained;

- module 3 (fig. 6) represents the unit for pumping of the phases decanted at the neutralization of spent caustic solutions from EXOMER unit;

- module 4 (fig. 7) represents the unit for pH correction of the resulted flow through mixing of waste waters from refinery with the spent caustic solution from MEROX unit and with the aqueous phase resulted at the deep neutralization of spent caustic solution from EXOMER unit.

First module, presented in figure 4, is dedicated to dilution and pumping of spent caustic solutions from MEROX installation. Caustic solutions are pumped with a metering pump with flow rate controlled by a flow controller, which ensures the dilution in the wastewater.

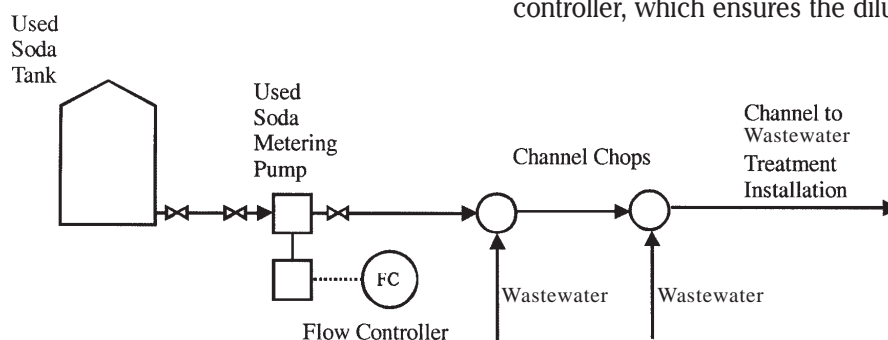


Fig. 4. Module 1 - The flow sheet of the installation for diluting and pumping of the spent caustic solution from MEROX

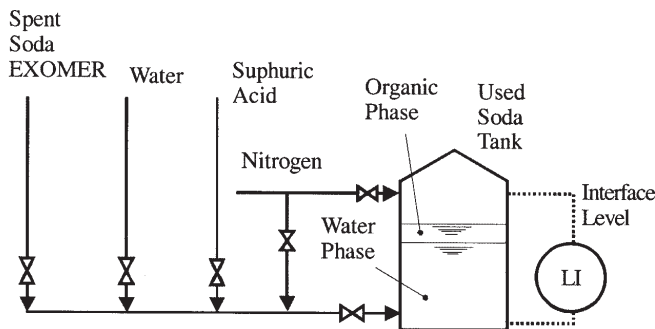


Fig. 5. Module 2 - The flow sheet of the installation for neutralization of the spent caustic solution from EXOMER and decanting of resulted phases

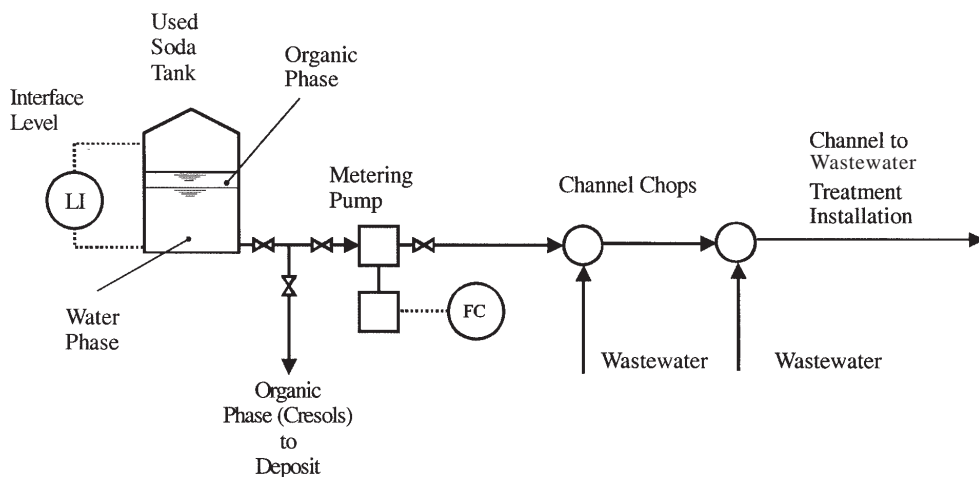


Fig. 6. Module 3 - The flow sheet of the installation for pumping of the decanted phases after neutralization of the spent caustic soda from EXOMER

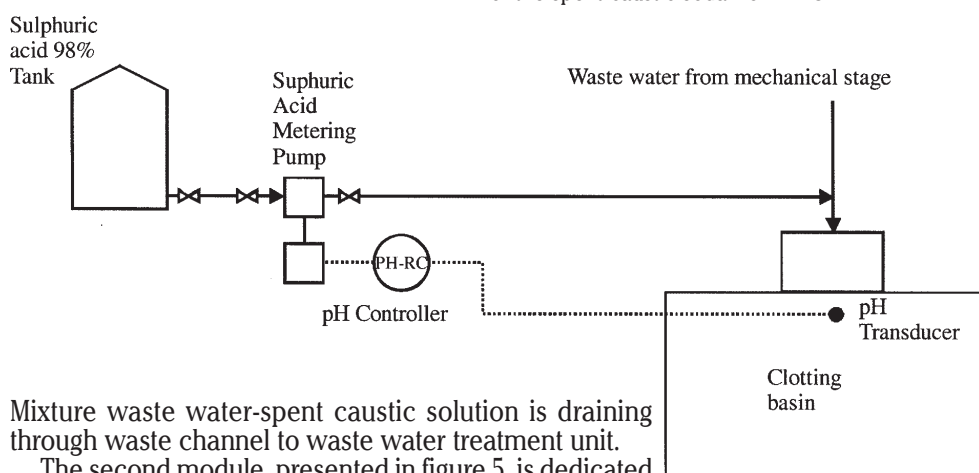


Fig. 7. Module 4. The flow sheet of the installation for pH control in wastewater treatment unit

Mixture waste water-spent caustic solution is draining through waste channel to waste water treatment unit.

The second module, presented in figure 5, is dedicated to neutralization and decanting of spent caustic solutions from EXOMER installation. The treatment is done in discontinuous regime, the spent caustic solution being brought in the treatment vessel. In the vessel is added water or condensed steam in a quantity appropriate to neutralization with a solution of 10% sulphuric acid. In the vessel is added sulphuric acid in a quantity required to achieve the final $pH = 2.0 \dots 2.5$. All operation are conducted under nitrogen pressure and stirring. After settling up to one hour the phases separated may be evacuated (Module 3 from fig. 6). The aqueous phase is send to waste channel with a metering pump controlled with a flow controller, achieving the dilution imposed. The organic phase is evacuated in an intermediary reservoir, from were it can be send to various uses.

Module 4 is presented in figure 7. Wastewaters from mechanical step of wastewater treatment unit that may contain both diluted caustic solution from MEROX and the organic phase from deep neutralization of spent caustic solutions from EXOMER installation are mixed with sulphuric acid whose flow rate is adjusted depending on the pH from the flocculation basin.

Experiment at industrial scale in continuous regime to validate proposed variant for spent caustic solution from MEROX

The experiment at industrial scale was conducted in continuous regime for some weeks using the industrial units presented in the previous section.

For entire period of experimentation were registered as average working parameters calculated based on the records of levels and rates:

Average flow rate of caustic solution	277 L/h
Average flow rate of acid	7.5 L/h
Average flow rate of wastewater	531 m ³ /h

The streams analysis was performed more often that provide the manufacturing control program.

The analysis of wastewater at input of wastewater treatment unit compared with maximum allowable values, shows that during the treatment the maximum allowable values were not exceeded.

Table 4
RESULTS OF THE INDUSTRIAL EXPERIMENTS FOR MEROX SPENT CAUSTIC SOLUTIONS TREATING (ANALYSIS OF WASTEWATER FROM REFINERY DURING THE USED SOLUTION PUMPING)

Nr.	pH	Base, %	Sulphide, mg/l	Phenols, mg/l	Ammonium, mg/l	CCOCr, mg/l	CBO ₅ , mg/l	Suspensions, mg/l	Extractible, mg/l
		total strong							
1	9.1	0.02 0.003	6.8	12.2	7.3	812.5	278.2	82	1860
2	6.75	0.008 0.0	9.1	11.8	7.0	657.0	204.5	123	1781
3	9.38	0.022 0.016	6.2	9.8	21.5	612.7	209.2	135	280
4	9.3	0.020 0.0044	5.8	10.4	14.3	604.6	102	142	167
5	8.3	0.05 0.0025	8.3	2.2				44	105
6		0.009 0.003	16.6	11.8	15.1	297	91	146	418.4
7		0.0198 0.0085	5.7	6.8	7.3	723	256.3	79	1892
8	7.8	0.010 0.002	5.4	7.2	7.8	682	238.4	75.1	1650
9		0.0153 0.0033	7.6	8.3	10.4	491	170.6	140.4	1537
10	9.28	0.018 0.006	5.8	10.2	9.2	912	324.6	142	2372
11	9.1	0.0173 0.006	8.4	10.4	10.4	890.8	290.4	149	1821
12	9.47	0.018 0.009	9.2	10.9	18.2	520.8	201.5	135	1598
13	8.8	0.0123 0.005	6.3	11.5	9.3	933	345	126	2782
14	7.68	0.0165 0.0	0.8	8.8	10.2	682.8	215.9	117	657.4
15	9.5	0.0199 0.008	9.7	12.6	15.7	987	395	111	2478
16	9.3	0.0185 0.007	9.3	11.5	16.2	977	390.4	105	2134
17	8.6	0.0195 0.006	10.3	10.3	15.7	966	401.5	115	1956
Admissible value	8.5		40	15	12	994		150	4000

Table 5
ANALYSIS OF THE STREAMS RESULTED FROM INDUSTRIAL EXPERIMENT FOR NEUTRALIZATION AND PUMPING OF THE SPENT CAUSTIC SOLUTION FROM EXOMER INSTALLATION

Nr.	Sample	pH	Sulphides, mg/l	Phenols, mg/l	Ammonia, mg/l	CCOCr, mg/l	Solid suspension, mg/l	Extractible, mg/l
1	Water phase decanted		1.9	6219	0.2	20168	930	1894
2	Waste water entrance	7.70	2.24	11.97	9.8	387.5	50	376
3	Waste water entrance	7.90	2.61	12.1	8.7	977.9	340	233
4	Waste water entrance	7.08	1.48	11.12	10.2	614.7	133	206
5	Waste water entrance	6.80	2.24	11.49	11.8	564.5	210	122
6	Waste water entrance	7.20	2.60	11.14	5.8	508.0	40	30
Admissible value		6.5-8.5	40	15	12	994	150	4000

Experiment at industrial scale for validation of the proposed variant for treating of the spent caustic solution from EXOMER through neutralization and mechanical separation

Acid treatment and homogenization were performed stirring the solution with nitrogen introduced at the bottom of the vessel. After the achievement of the wanted pH value, the aqueous solution was allowed to decant for 15-20 min.

Decanted solution was then pumped with a metering pump in the wastewater network.

The analysis of the wastewater at incoming of the wastewater treatment unit compared with the maximum allowable values show that during the treatment these maximum allowable values were not exceeded.

Globally experiment at industrial scale for validation of the proposed variant for treating of the spent caustic solutions both from MEROX and EXOMER units

The final part of the experiment consists in neutralization and dilution of both spent caustic solutions, MEROX and EXOMER. Through pumping of the spent caustic solution from MEROX unit simultaneously with the aqueous phase resulted at the deep neutralization of the spent caustic solution from EXOMER unit in the wastewater channel we wanted to validate the proposed technology. In table 6 are presented the results of this experiment.

Analysis of waste waters at the incoming of the waste water treatment unit and the analysis of the treated water

Table 6
ANALYSIS OF RESULTED STREAMS FROM THE INDUSTRIAL EXPERIMENT FOR BOTH SPENT
CAUSTIC SOLUTIONS FROM MEROX AND EXOMER UNITS

Nr.	Sample	pH	CCOCr, mg/l	Sulphides, mg/l	Phenols, mg/l	Ammonia, mg/l	Chlor, mg/l	Suspension, mg/l	Extractibile, mg/l
1	Water phase	2.2	23040	23.94	5243.1	0.21	94.6	-	-
2	Waste water input	8.2	384.4	0.25	16.84	9.31	118.2	-	-
3	Output water	6.7	67.2	0.06	0.183	1.75	95.7	57	16
4	Waste water input	8.5	624	0.16	16.61	9.88	120.3	-	-
5	Output water	6.4	52.8	0.06	0.187	0.46	76.5	54	16
6	Waste water input	7.2	441.6	1.82	23.62	3.81	98.7	-	-
7	Output water	6.9	38.4	0.06	0.154	1.5	106.4	45	18
8	Waste water input	6.8	787.2	2.13	20.32	4.56	140.5	-	-
9	Output water	6.6	28.8	0.17	0.254	1.26	112.3	56	16
10	Output water	6.9	0	0.05	0.283	1.12	78.4	42	12
Allowable value input		6.5-8.5	994	40	3.16			150	4000
Allowable value output		6.5-8.5	125	0.5	0.3	2		60	20

at the exit of the treatment unit, compared with the maximum allowable values, show that during the treatment the maximum allowable values were not exceeded.'

The main purposes of the experiments were to prove at industrial scale that the proposed technology based on the laboratory study :

- it is viable;
- does not affect the functioning of the waste water treatment unit;
- does not modify significantly the quality of treated water.

The evaluations from technological and ecological point of view of proposed solution lead to the next conclusions:

- the contaminants present in used soda are diluted and neutralized up to maximum allowable values permitted by the legislation;
- the neutralization does not generate gaseous or solid byproducts; all products are soluble and can be treated in wastewater treatment station;
- treatment station does not suffer a significantly charge which can lead to decreasing performance or increasing costs;
- it does not exceed the maximum allowable values provided by PCA into the wastewater treatment station;
- solutions utilized for neutralization are not dangerous for employees and from an environmental protection point of view; sulphuric acid handling is known and does not bring any problems if rules are respected;
- dilution and neutralization are simple operations that do not need expensive and pretentious equipment or additional staff with special qualifications;
- totally, the process is simple, safe, and accurate;

- apparition of some risks of ecologic nature is extremely reduced, even in eventuality of equipment malfunction; unit stopping , even with lateness, ensure that any risks of pollution are eliminated.

Conclusions

The paper presents:

- the industrial installation proposed by authors for treatment and removal of the spent caustic solution from refineries;
- laboratory experiments and industrial test concerning the dilution and the neutralization of the spent caustic solution from MEROX units;
- laboratory experiments and industrial test concerning the neutralization and the separation of the spent caustic solution from EXOMER units;
- treatment of the resulted solution in an industrial wastewater plant;

The process and the installation are subject of a Romanian patent demand [3].

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