



USING SOME PHYSICAL CHEMICAL METHODS IN THE CONTROL OF THE ACID WATERS FROM STORAGE BATTERIES MANUFACTURES

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abstract: In this work residual acid waters samples from two storage batteries manufactures were studied. The samples from Acumulatorul SA prelevated in two periods were studied by pH-metric method, conductimetry and densitometry. The samples from Autoservice Caranda were studied only by pH-metric and conductimetric methods. The characteristics of both stations for residual water treatment were discussed and evidenced.

key words: acid residual waters; neutralisation stage; conductimetry method; pH-metric method; densitometry method.

received: June 14, 2010

accepted: June 19, 2010

1. Introduction

Relationship between uses and water quality requirements is fundamental. The principal water uses are for drinking, irrigation, industrial processing and as heat transfer agent [1]. Because the volume of water included in artificial cycle is increasing, being a significant part from the total volume of “sweet” water [2], a modern water industry is claimed. This industry comprises treatment and recycling installations, installations for water transfer from different geographic zones, for iceberg exploiting, for desalinisation etc. [3].

Considering the environmental impact due to waste waters from batteries storage manufactures provenience were examined the technological process basis in such companies and the possibility of treatment and control [4]. Batteries storage industry possesses a high development perspective in view accumulator uses in urban and interurban transport.

The residual waters resulted from specific manufactures must accomplish the requirements of corresponding STAS [5], concerning acidity and salts content.

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In this paper the results of physical–chemical measurements effected on acid waters samples with provenience from Acumulatorul SA and Autoservice Caranda were examined. The first company assumes Romanian tradition of SAR Tudor, founded in 1911, passing over much changes until present. Acumulatorul SA posses now a production capacity of 1320 Mwh, trading over 150 types of batteries. Autoservice Caranda is a small manufacture for auto-accumulators, founded after 1995. We considered oportune the study of residual waters before and after neutralisation stage by some global physic-chemical methods, which have a reduced cost and accessibility in such companies for operators with medium qualification.

Experimental

Materials

The water samples from Acumulatorul SA are harvested before and after neutralisation stage (in which are included the waters from *Plates Formatation* and *Plates Washing & Drying* sections in two periods: January 2004 and March 2004) as results from Tables 1, 2. The water samples from Autoservice Caranda were prelevated in the same mode in May 2004 (Table 3). For each sample a volume of 500mL was harvested, enough to assure accuracy and reproducibility for all tests. For estimation of conductimetric constant cell values 1L of 1n KCl aqueous solution are prepared using KCl Merck p.a. and double distilled water. From this solution by dilution were obtained needed quantities of n/10 and n/100 KCl solutions which have standard values for specific conductivity [7]. For conductimetric titration a 0.01nNaOH solution was prepared in the same mode.

Apparatus

pH was determined with indicator paper Merck having a precision ± 0.5 units of pH.

Density was measured with an areometer, etaloned at 20°C, characterized by precision $\pm 0.001\text{g/cm}^3$.

The conductivity measurements are effected with conductimeter LTB (Seibold, Austria) which possess two measuring immersible cells LZ1, LZ10 and a thermal compensator. These cells no need customary platination [7-10]. At this instrument can be connected a supplementary instrument for registration. Specific electric conductivity γ , expressed in $\mu\text{S}\cdot\text{cm}^{-1}$, is done by following relation:

$$\gamma = K \cdot G \cdot 10^3 \quad (1)$$

where K is conductimetric constant cell (determined as $1.19\text{C}\cdot\text{cm}^{-1}$ for LZ1 cell)

G-measured electrical conductivity.

Measurement protocol

The measurements were effected in laboratory taking samples of residual waters to Berzelius glasses which were beforehand rinsed with a small quantity from studied water. Then, LZ1 cell was introduced with all three platinum rings under liquid surface. After this, the value of G was selected on the proper conductimetric scale.

Results and discussions

In the Tables 1-3 the samples with numbers 1-4, 11-13, 17-19 are referred to acid waters before neutralisation stage and the samples with numbers 5-10,14-16 correspond to neutralised waters. The value of specific conductivity from third columns in the Tables 1 and 2 are referred for 12°C or 13 °C and those from 4th columns to laboratory temperature.

Table 1 *Physical –chemical measurements of residual waters (harvested at 22.01.2004).*

Sample number	pH	$\gamma(\mu\text{Scm}^{-1})$ at 12 °C	$\gamma(\mu\text{Scm}^{-1})$ at 22C	ρ (g/cm ³)
1	3.5	2.14	2.62	0.998
2	3	3.57	3.57	1.000
3	3	3.33	3.33	0.999
4	4	2.86	2.85	0.999
5	6	9.99	9.28	1.000
6	6	10.47	9.52	1.000
7	6	9.52	8.33	1.000
8	6	10.35	9.52	0.999

Table 2 *Physical –chemical measurements of residual waters (harvested at 31.03.2004).*

Sample number	pH	$\gamma(\mu\text{Scm}^{-1})$ at 13° C	$\gamma(\mu\text{Scm}^{-1})$ at 22C	ρ (g/cm ³)
9	6	11.31	11.54	1.000
10	6	11.54	11.50	0.998
11	3.5	4.46	4.46	0.998
12	3	3.81	3.57	1.000
13	3.5	4.17	3.69	0.999

In the case of Table 3 concerning the same type of data from Autoservice Caranda no differences between external and laboratory temperature values of conductivity and number of used physical-chemical used methods in investigation is restrained.

Table 3 *Physical –chemical measurements of residual waters (obtained at 05.05.2004).*

Sample number	pH	$\gamma(\mu\text{Scm}^{-1})$ at 21 C
14	6	7.14
15	6	8.09
16	8.5	9.28
17	2	3.21
18	2.5	4.16
19	3.5	2.38

From analysis of experimental data it is obvious that after addition of NaOH neutralisation process is managed until a weak acid pH. The reason for this is hindrance of precipitation

of different metallic ions (Pb, Zn, Fe) presents in solutions. It is also obvious that neutralised residual waters have a 3 once increased electrical specific conductivity due to increased numbers of ions in solutions. From the examination of the experimental data comprised in Tables 1 and 2 it is obvious that density no changes significantly between acid and neutralised waters, being nearly of water density ($\rho=0.999\text{g/cm}^3$), which depends on temperature. Dilution is so managed to no affect weight transfer in installations.

For the sample 3 it is realised also a conductimetric titration (see Table 4).

Table 4 *Conductimetric titration of the sample 3 ($V_s=135\text{ mL}$).*

Current number	G(S.m ⁻¹)	VNaOH 0.1n(mL)
1	2.8	0
2	3.2	0.3
3	2.8	0.6
4	2.6	0.9
5	2.5	1.2
6	2.7	1.2
7	3.0	1.8
8	3.4	2.1
9	3.7	2.4
10	4.0	2.7
11	4.4	4.0
12	4.7	4.3
13	5	4.6
14	5.4	4.9
15	5.7	5.2
16	6.3	5.5
17	6.5	5.8
18	6.8	6.1
19	7.2	6.4
20	7.5	6.7
21	7.7	7.0
22	7.6	7.3
23	8.0	7.6
24	8.2	7.9
25	8.6	8.1
26	9.0	8.4

Aim of this titration was to detect the quantity of sulphuric acid in these acid waters.

From pH value of this sample we obtain the following information:

Because $pH = 3$ results $[H] = 10^{-3}$ equivalents gram/L or mol/L. This result is in accord with data obtained from conductimetric titration.

The needed NaOH quantity for neutralisation at this pH is in conformity with following equation:



equal with $80 \cdot 10^{-3} g NaOH/L$ (or $0.08 kg NaOH/m^3$) From analysis of diagram $G(mS)-f(VNaOH, mL)$ corresponding to Table 4 data obtained for titration of volume V_x results volume at equivalence $V_E = 3.9 mL NaOH 0.1n$.

In conformity with well known identity: $V_x C_x = V_E C_E$

Results $C_x = 0.0028$. This means that approximate concentration of sample 3 is $3 \cdot 10^{-3} n$, which correspond to $0.147 g H_2SO_4/L$. The detection of sulphate anion methods in waters are object of recent research [11-14] underling importance of conductimetric method in monitoring of the polluted waters.

Conclusions

1. In this work the samples of residual acid waters collected before and after neutralisation stage from manufactures Acumulatorul SA and Autoservice Caranda are studied.
2. The samples from Acumulatorul SA are harvested in two periods: January and March 2004 and were studied pH -metric, conductimetric and by densitometry. For one sample was effected also a conductimetric titration for quantitative determination of acidity. The processed waters in Acumulatorul SA correspond to second category of surface waters in conformity with actual UE reglementations, but treatment station is complex, old and difficult to maintain in parameters.
3. The samples harvested in May from Autoservice Caranda were studied only by pH -metry and conductimetric methods. The corresponding treatment of residual waters station is dimensionally reduced, new and automatized.

Aknowledgements. First author thanks to leaders of Human Resource Office from Acumulatorul SA and Autoservice Caranda for permitting access to technical documentation and samples furnishing in the period January to May 2004 of the practical work to bachelor thesis .

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