NICKEL RECLAIMING FROM GALVANISING RESIDUAL WATERS

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INTRODUCTION

As far as reclaiming, recycling and reuse of wastes are concerned, the used concentrates and galvanic waste water have to be treated in two ways: on one side for the used waters reclaiming and re-circulation for water consumption reducing, and on other side for reclaiming the useful substances contained in the waste waters.

The present paper presents studies concerning nickel reclaiming from used waters (UW) resulting from galvanisation through precipitation with sodium hydroxide. The successive aims were as follows: galvanising UW characterisation from the physical-chemical point of view; nickel precipitation from the used solution; there has been traced the precipitation(neutralisation) curve of the solution; there has been followed the sedimentation rate of the precipitate as time function; and there has been made the analysis of cakes obtained after precipitate filtering. At the same time, studies have been carried out concerning nickel hydroxide cakes re-dissolving with sulphuric acid.

Nowadays, when due to industrial development there result ever greater volumes of UW, it is imperative to treat these waters before their release in the receiving waters. Moreover, the separate treatment of UW that result from each workshop separately will have to be carried out, because it is known that the more UW is loaded, the more difficult its treatment will be accomplished. At present, at nickel plating technology, the electrolyte exhausted solution of the galvanic baths is replaced once in three months, a fact that brings about discharge problems. Under the circumstances, the present paper discussed nickel reclaiming from used UW from galvanising shops as well as the reduction of these UW through their re-circulation.

EXPERIMENTAL

The analysis of the used galvanising solution was carried out, in the first stage, knowing the electrolyte initial composition: nickel sulphate, nickel chloride, basic acid and neutral salt (salt cake or potassium sulphate).

Precipitation studies, with NaOH, 20%, were carried out with the original electrolyte, a synthetic electrolyte, with or without polishing agents, and with a mixture obtained by mixing an exhausted electrolyte volume with the same volume of rinsing water from the first rinsing stage. This mixture was also analysed from the chemical point of view. pH interval when the precipitation takes place was also deduced. The experiments were continued with samples of 50 ml. mixture of used solution to which there were added NaOH 20% doses corresponding to a pH range between 8.75 – 10.5, with the simultaneous following of the precipitate sedimentation rate as well as the concentration of the residual nickel from the supernatant.

Humidity was determinate by taking samples of 50 ml. precipitate which was filtered and dried for three hours at 105 °C. For filterability determining it was not the coefficient of permeability which

was determinate, but the resistance to filtering which is the reverse permeability coefficient. With a view to characterise the cakes from the point of view of the nickel contents, they were dissolved with sulphuric acid 25% at 50 °C, under continuous stirring, and then analysed with adequate methods. In order to study the re-dissolving conditions for these cakes, there was studied the concentration of the solutions obtained at their treatment with various quantities of sulphuric acid 25%(in all cases the used quantity of H_2SO_4, 25% has been in excess as compared to the stoechiometric one).

Since after the precipitation there still exists residual nickel in the filtered solution, it has to be removed from the solution. To carry out this removal, there was used a filter equipped with chemically modified zeolite under the form of sodium. The clinoptilolitic zeolite used came from Mirsid deposits-in north-west Romania.

RESULTS AND DISCUSSIONS

Following the chemical analysis of the exhausted electrolyte from galvanisation and that of the exhausted electrolyte from galvanisation and that of the exhausted electrolyte mixture and washing water, there were obtained the compositions described in Table 1.

Table 1. The chemical composition of the exhausted electrolyte and that of the
electrolyte – washing water mixture

Parameter	Ni^{2+} [g/l]	Cl^- [g/l]	H_3BO_4 [g/l]	pH
Exhausted electrolyte	64.13	12.78	29.87	3.02
Electrolyte and washing water mixture	37.50	9.94	20.50	6.20

The results obtained through NaOH 20% precipitation enabled the tracing of the neutralisation (precipitation) curves is illustrated in figure 1(a, b, c, d).
Figure 1 shows that pH interval, when the precipitation takes place, is of 8.75-10.30, not being influenced by the presence of polishing agents. The optimum dose of NaOH 20% to be added is established in this pH interval, the results being presented in table 2.

Table 2. NaOH 20% optimum dose establishing

Sample no.	1	2	3	4	5
NaOH dose/ 50 ml sample	15.0	15.6	16.5	17.5	18.5
PH	8.75	9.2	9.5	10.3	10.5
Residual Ni^{2+} [g/l]	0.85	0.45	0.2	0.15	0.14
Efficiency	97.6	98.70	99.45	99.6	99.62

The efficiency of Ni^{2+} removal process from UW from galvanisation, as function of NaOH 20% dose addition is illustrated in figure 3.
Thus, the optimum dose of NaOH 20% is of 17.5 ml at 50 ml, which corresponds to a consumption of 7 kg NaOH at 100 L used solution. The sedimentation curves also show that the use of the precipitate separation of the solution through simple decantation is not economical, the sedimentation rate being not a significant one.
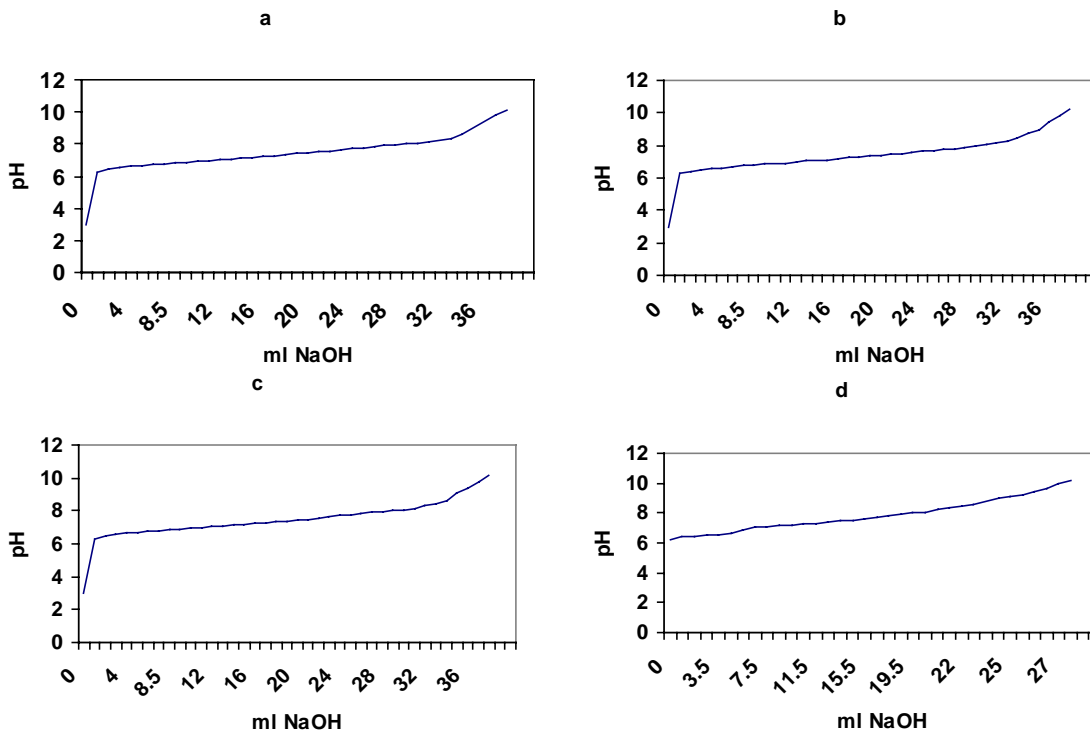
Figure1. NaOH 20% precipitation curves for:
a) original electrolyte
b) sinthetical electrolyte without polishing agents addition
c) sinthetical electrolyte with polishing agents addition
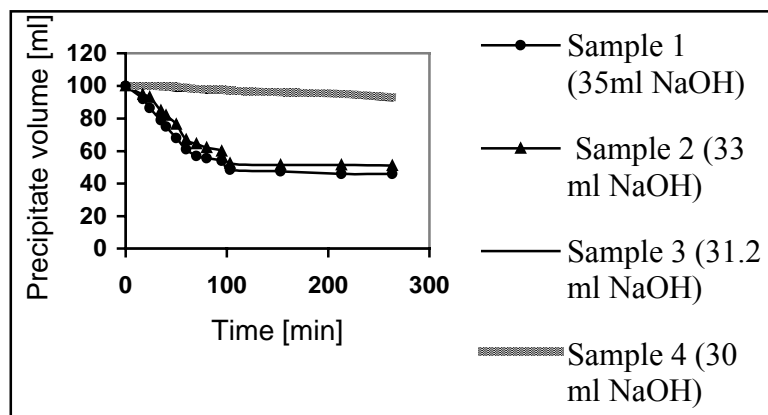d) mixture of original electrolyte and water from the first washing

Figure 2. Presents the sedimentation curves of the nickel hydroxide precipitate, as function of used pH.

Following the vacuum filtering of the precipitates there were obtained cakes-a part of which were dried in the drying chamber at 105 °C, and others were capted several weeks to be air dehydrated and for the precipitate ageing. Table 3 presents the properties of dried and wet cakes.
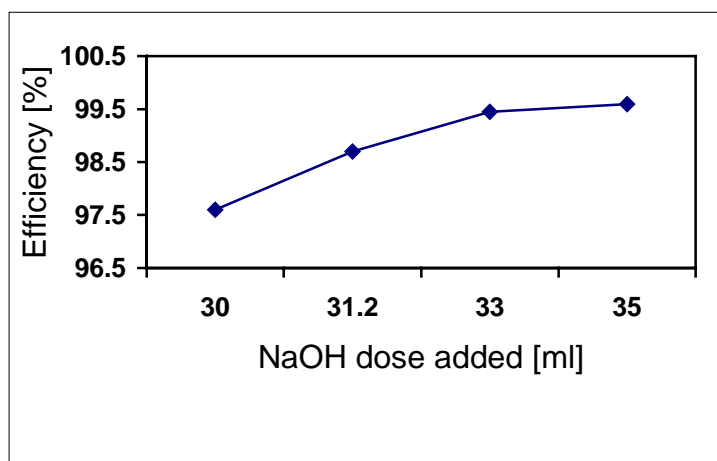
Figure 3. Efficiency of Ni 2+ retaining process as function of NaOH dose.

Table 3. The physical properties of the precipitate cakes

Property	New precipitate from the synthetic electrolyte	Aged precipitate from the synthetic electrolyte	Electrolyte precipitate
Humidity [%]	79.23	65.00	75.55
Density [g/cm^3]	1.12	1.12	1.28

The figure 4 illustrates the graphical representation Time/Volume = f(Volume) obtained after the filterability tests results at the pressure of 100 mm Hg. The procedures employed were similar for pressures of 200 and 300 mm Hg. Table 4 presents the working pressures as well as the specific resistance.

Table 4. Specific resistance of the cake at various pressures

Pressure P [mmHg]	100	200	300
R [cm/g]	$1.174 \cdot 10^{10}$	$1.728 \cdot 10^{10}$	$4.509 \cdot 10^{10}$
log P	5.12	5.42	5.60
log r	10.06	10.23	10.65

The dependence between log r = f(log P) is presented in figure 5, and as compressibility coefficient can be deduced from the line slop. [S = log r/log P=1.16].
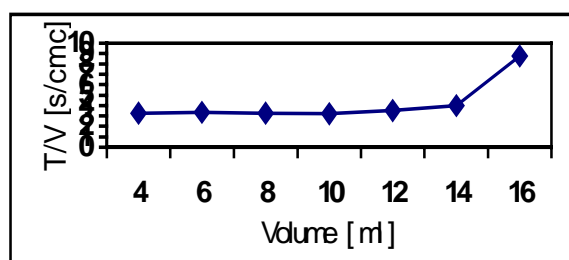

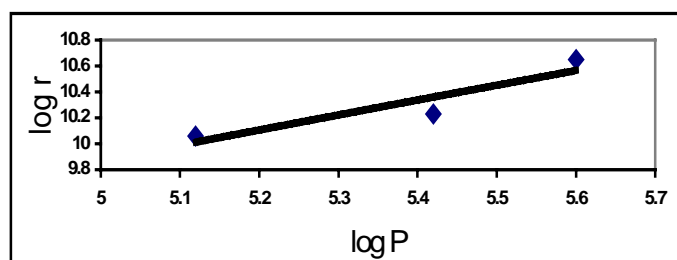Figure 4. The dependence T/V=f(V) obtained at the pressure of 100 mm col. Hg

Figure 5. Log r and log P interdependence

After the determinations carried out on the dried cake and on the wet cake, respectively there was established that nickel concentration in the wet cake is of 3.46%, and in the dried cake it is of 36.7%, these being obtained from the electrolyte and washing water mixture.

Table 5 presents the redissolving conditions of wet cakes and dried cakes, respectively.

Table 5. Redissolving conditions for the wet cake

	Kind of cake						
	Wet			Dried			
Cake weight [g]	10	10	10	1	2	3	4
H_2SO_4 25% [ml]	50	25	12.5	50	50	50	50
Ni^{2+} concentration [g/l]	7.34	13.2	15.56	6.9	14	19.5	66.7

The solution that results after filtering contains residual Ni^{2+} in the interval(0.15-0.8)g/L; in order to eliminate Ni^{2+} traces there was used a filter equipped with chemically modified zeolite, under the form "sodium", which retains the nickel through ionic exchange. Exhausted zeolite regeneration is carried out with NaCl 10%.

CONCLUSIONS

After the experimental studies that were carried out as mentioned in the present paper, the following conclusions can be drawn out:

1. It has been observed out of the comparative study carried out on the exhausted original electrolyte, on the synthetic electrolyte with polishing agents addition and on the synthetic electrolyte without polishing agents addition, and on the electrolyte-washing water mixture, that the presents of the polishing agents does not disturb the precipitation process which takes place between the following values: 6.5 – 10.0;
2. By treating an exhausted electrolyte and washing water mixture (in equal volumes) with NaOH 20% solution, we can conclude that the precipitant optimum dose corresponds to a consumption of 7 kg NaOH at 100L used solution mixture;
3. The efficiencies of the precipitation process are high, arriving at 99.6%.
4. Following the physical-chemical analyses of the precipitate cakes obtained after the study of nickel redissolving with H_2SO_4 25% there was observed that cakes filtering drying and ageing are more convenient, after which the re-dissolving with H_2SO_4 25% can be carried out.
5. Following the studies carried out and using the above given conclusions there can be proposed an operational diagram of a nickel plating installation with the integral recycling of the nickel form the used solutions and with the reuse of the residual waters in the washing process.

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