

Use of Surfactants to Reduce Release of Nickel Aerosols during Nickel Electrolysis*

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Abstract

A trial test procedure has been devised for testing the properties of surfactants to be used as additives to reduce nickel aerosol concentrations in the air of the working site in nickel electrorefining. More than 50 various surfactants from Russian and foreign manufacturers have been tested. Good aerosol suppression is demonstrated by "Chromin" (potassium ethylcyclohexanepfluorosulphonate), "Progress" (secondary sodium alkylsulphate), and "Sulphonole" (sodium alkylbenzozsulphonate) surfactants, which do not cause deterioration of cathodic nickel.

INTRODUCTION

During electrolytic production of some heavy non-ferrous metals, aerosols are released into the atmosphere of the plant, polluting the environment and accelerating corrosion of metallic details. An illustrative example is electrolytic production of nickel where emission of aerosols from the surface of electrolysis bath solution increases the nickel content in the air of the working site (AWS) to 0.5–1.5 mg/m³, which considerably exceeds the maximum permissible concentration (MPC) (0.005 mg/m³) [1].

Various methods are used to control the emission of nickel aerosols into the AWS of electrolysis departments [2] at plants where non-ferrous metals are produced electrolytically. One of these methods is covering the surface of electrolyte with a layer of foam, resulting from the addition of a surfactant.

The assortment of currently available foaming surfactants is reasonably wide [3, 4]. However, to choose a surfactant, one should take into account that electrolysis processes are very

sensitive to the presence of organic compounds in the electrolyte [5].

The diversity of opinions about the mechanisms of surfactant action on metal electrodeposition processes hinders selection of surfactants with required properties. Selection is often empirical and hence time-consuming. In addition to electrolysis, nickel electrorefining involves a number of refinement operations to remove Cu, Fe, and Co impurities from the nickel-bearing electrolyte, which makes it necessary, when selecting the surfactant, to take account of its interference with cathodic precipitation of nickel and with the properties of electrolyte.

METHODOLOGY AND PROCEDURE OF LABORATORY TESTS

To simplify selection of foaming surfactants having no negative effects on nickel electrorefining processes and reducing hydroaerosol release from the surface of electrolyte, a comprehensive trial test procedure has been devised (Fig. 1). It involves five major steps.

1. Investigation of surfactant solubility.

2. Investigation of surfactant effects on the properties of the electrochemical system.

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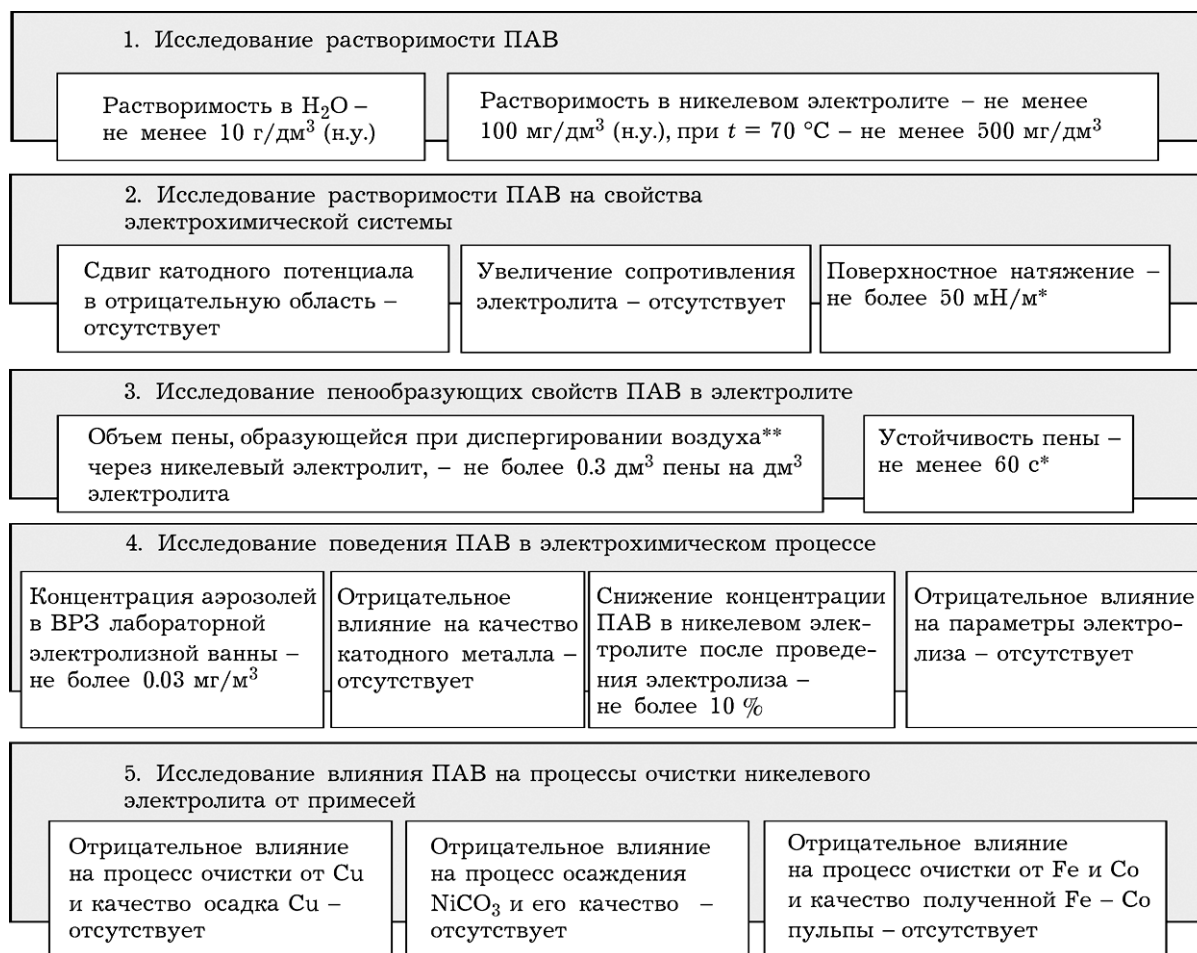


Fig. 1. Schematic diagram showing stage-by-stage comprehensive laboratory tests to examine the applicability of a surfactant as an aerosol suppression additive to nickel-bearing electrolyte: *at a concentration of surfactant in electrolyte of 50 mg/dm³, **at an air flow rate of 1 l/min per 1 litre of electrolyte with the surfactant added.

3. Investigation of the foaming properties of the surfactant in the electrolyte.

4. Investigation of surfactant behaviour in an electrochemical process.

5. Investigation of surfactant effects on purification of the nickel-bearing electrolyte from impurities.

The first, second, and third steps were carried out by the known procedures [6–8]. The first four steps employed nickel-bearing electrolyte that was equivalent in its chemical composition to the catholyte of the nickel electrolysis department (NED) of “Norilsk Nickel”, g/dm³: Ni²⁺ 70; Na⁺ 25; SO₄²⁻ 120; Cl⁻ 37; H₃BO₃ 2; pH 2.5.

Investigations of surfactant effects on nickel electrolysis were performed with a laboratory electrolysis setup (Fig. 2). Plates of cathode nickel of N-1 grade (GOST 849–97)

were used as electrodes. The “Polyester” fabric, mark 71-2255-V5, served as a diaphragm material.

Electrolysis was performed at a cathode current density of 250 A/m², electrolyte circulation rate of 25 dm³/(A h), and electrolyte temperature of (70 ± 2) °C.

Cathode deposit growth time was 72 h. Sampling of AWS was made with an M-822 aspirator. The samples were analyzed for the nickel content according to the known procedure of photocolometric determination of nickel concentration [9]. Residual surfactant concentration in electrolyte was determined photocolometrically with Azur A indicator after surfactant extraction with chloroform from the nickel-bearing electrolyte [10]. The quality of cathode nickel obtained by electrolysis was assessed according to GOST 849–97.

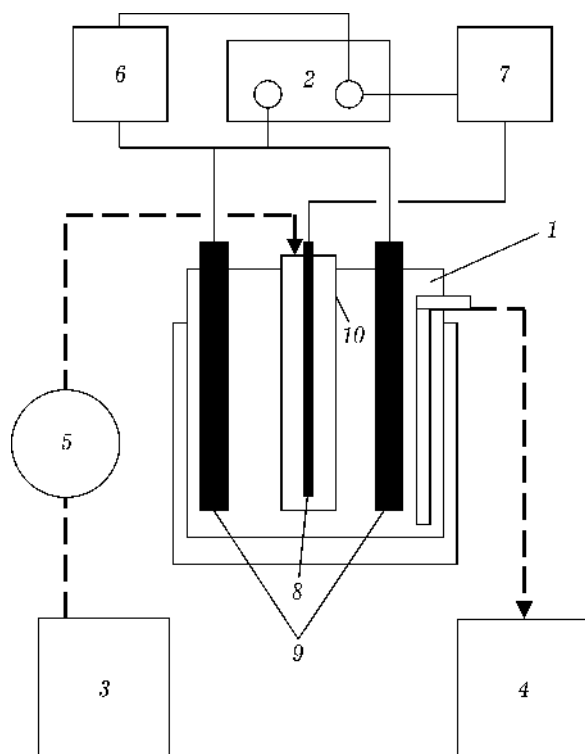


Fig. 2. Schematic diagram of a laboratory electrolysis setup for investigating surfactant effects on nickel electrolysis: 1 – 2.7 dm³ temperature-controlled electrolysis bath; 2 – VSA-5 rectifier; 3, 4 – tanks for the initial and waste electrolytes, respectively; 5 – “Masterflex – 7553-85” peristaltic pump; 6, 7 – M2038 voltammeters; 8, 9 – nickel electrodes; 10 – diaphragm cell.

The surfactant effects on decontamination of nickel-bearing electrolyte from Cu, Fe, and Co impurities were studied using the regimes listed in Table 1.

The limitations inferred from previous experience and imposed on each step of investigation allowed us to draw conclusions about the utility of surfactants and to decide upon the necessity of studies at next steps.

1. Insufficient water solubility (less than 1 g/dm³ at 20 °C) complicates surfactant dosing when the surfactant is introduced into the nickel-bearing electrolyte.

2. Insufficient solubility in the nickel-bearing electrolyte (less than 100 mg/dm³ at 20 °C and less than 500 mg/dm³ at 70 °C) results in worse technological parameters of nickel electrolysis and electrolyte decontamination from impurities.

3. The shift of cathode potential to the negative region and decreased electric conductivity of electrolyte in the presence of surfactant result in additional power consumption during electrolysis.

4. Intense foaming (more than 0.3 of the foam volume per volume of electrolyte) precludes the use of the surfactant in nickel electrorefining technology because foam overflows

TABLE 1

Laboratory regimes of investigation of surfactant effect on decontamination of nickel-bearing electrolyte from Cu, Fe, and Co impurities

No.	Operation	Basic modes	Composition of starting materials
1	Decontamination from copper through reduction with nickel powder	$\tau = 3$ h, $t = 70$ °C, pH 2.0, consumption of nickel powder (ratio between the quantity of active nickel in the powder and the stoichiometric quantity of copper in the solution) is 120 %	Concentration of electrolyte: g/dm ³ : Ni ²⁺ 65, Cu ²⁺ 1.5, SO ₄ ²⁻ 120, Cl ⁻ 37; active nickel content in the powder is no less than 80 %
2	Precipitation of nickel carbonate with a Na ₂ CO ₃ solution	$\tau = 1$ h, $t = 80$ °C, pH 8.5, mechanical stirring	Concentration of electrolyte, g/dm ³ : Ni ²⁺ 70; SO ₄ ²⁻ 120; Cl ⁻ 37; pH 2.0; concentration of the Na ₂ CO ₃ solution is 200 g/dm ³
3	Decontamination from iron and cobalt through precipitation by Cl ₂ with NiCO ₃	$\tau = 2.5$ h, Cl ₂ supply time is 0.5 h, $t = 70$ °C, pH 4.0, rH = 1100 mV, mechanical stirring	Concentration of electrolyte, g/dm ³ : Ni ²⁺ 70; SO ₄ ²⁻ 120; C ⁻ 37; Co ²⁺ 0.4; Fe ²⁺ 0.8; NiCO ₃ content in the pulp is 300 g/dm ³

the chemical reactors of electrolyte decontamination.

5. Insufficient decrease in the surface tension of electrolyte (by less than 25 mN/m), high level of nickel aerosol release into the AWS of the electrolysis bath (more than 0.03 mg/m³), and low foam stability (less than 60 s) are indicative of surfactant inefficiency as an aerosol suppression agent.

6. Adverse surfactant effects on the parameters of electrolysis and decontamination, as well as deterioration of the cathode metal and high degree of surfactant decomposition, make the use of the surfactant in nickel electrorefining technology economically inexpedient.

More than 50 various surfactants from Russian and foreign manufacturers have been tested according to this procedure.

Only 25 % of all tested surfactants met the requirements imposed on selection. Unfitness of more than 40 % of all surfactants was revealed at the first stage of investigations; it was due to the insufficient solubility of the surfactant in highly ionized electrolyte solutions. One fifth of all tested surfactants had adverse effects on the quality of the cathode metal: easier pitting process, growth of needles, flaking-off of the cathode deposit from the substrate; about 8 % of surfactants decomposed partially or completely during electrolysis.

Characteristically, all surfactants suitable for nickel electrorefining belong to the class of anionic surfactants – sulphonates (R–O₃X) or alkylsulphates (R–O–SO₃X), where R is a hydrocarbon radical, and X is an alkali metal.

After pilot trials, three surfactants commercially available in Russia were recommended for use as aerosol suppression additives in cathode nickel production. These are perfluorinated potassium ethylcyclohexanesulphonate $n\text{-C}_n\text{F}_{2n+1}\text{C}_6\text{F}_{10}\text{SO}_3\text{K}$ (“Chromin”), secondary sodium alkylsulphate $\text{C}_n\text{H}_{2n+1}\text{CH}(\text{CH}_3)\text{OSO}_3\text{Na}$ (“Progress”) and sodium alkylbenzosulphonate $\text{C}_n\text{H}_{2n+1}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ (“Sulphonole”).

RESULTS OF PILOT TEST

Pilot test was conducted in a 1.2 m³ electrolysis bath equipped with two standard nick-

el cathodes with dimensions 880 × 1000 mm. The cathodes were placed into diaphragm cells from “Polyester” fabric (71-2255-V5 mark) at a current density of 220 A/m² and a temperature of (70 ± 2) °C in a NED electrolyte, which was free from impurities and fed to the cathode diaphragm cell at a flow rate of 25 dm³/h. Industrial crude nickel anodes from NED served as anodes. AWS samples of the electrolysis bath were taken and analyzed for nickel by procedures similar to laboratory ones. Test data are given in Table 2.

Evidently, the use of these anionic surfactants allows the concentration of nickel aerosols in AWS to be reduced by a factor of 10–20. These surfactants have a number of advantages. Thus “Chromin” shows the greatest stability against decomposition in electrolysis and decontamination of nickel-bearing electrolyte from impurities. Its concentration in the electrolyte does not change even after 12 turnover cycles of electrolyte, while the concentrations of “Progress” and “Sulphonole” decrease by 50 and 30 %, respectively, after six cycles.

According to literature data [11], the highest rate of biological decomposition is characteristic of “Progress”. It has no hydrocarbon ring chains in its structure, which makes the use of this surfactant more practical from ecological viewpoint in case of its accidental release in wastewaters.

“Sulphonole” has the highest aerosol suppression effect, and its specific consumption during nickel electrorefining is 0.033 kg/t of cathode nickel, whereas for “Chromin” and “Progress” consumption is 0.081 and 0.120 kg/t, respectively.

All surfactants for which pilot trials showed positive results were consecutively put to production at the NED of “Norilsk Nickel”. The annual average concentrations of nickel aerosols in AWS of NED according to the data of Norilsk sanitary and epidemiologic agency are presented in Fig. 3. It can be seen that the use of these surfactants allows the concentration of nickel hydroaerosols in AWS of NED to be reduced to 0.053–0.164 mg/m³.

A reduction of 10 % in the concentration of nickel aerosols in the AWS in 1999 compared to the level before 1990 is caused by the

TABLE 2

Results of pilot test of surfactants in the course of nickel electrorefining

Surfactant	Surfactant concentration in the electrolyte, mg/dm ³	Concentration of nickel aerosol in AWS of the electrolysis bath, $\frac{\text{min} - \text{max}}{\text{medial}}$, mg/m ³
–	0	0.261 – 0.405 0.333
Chromin	10	0.075 – 0.208 0.095
	20	0.043 – 0.119 0.068
Progress	10	0.085 – 0.185 0.094
	20	0.015 – 0.103 0.034
	40	0.015 – 0.113 0.039
Sulphonole	5	0.006 – 0.062 0.028
	10	0.005 – 0.035 0.026
	20	0.005 – 0.051 0.025

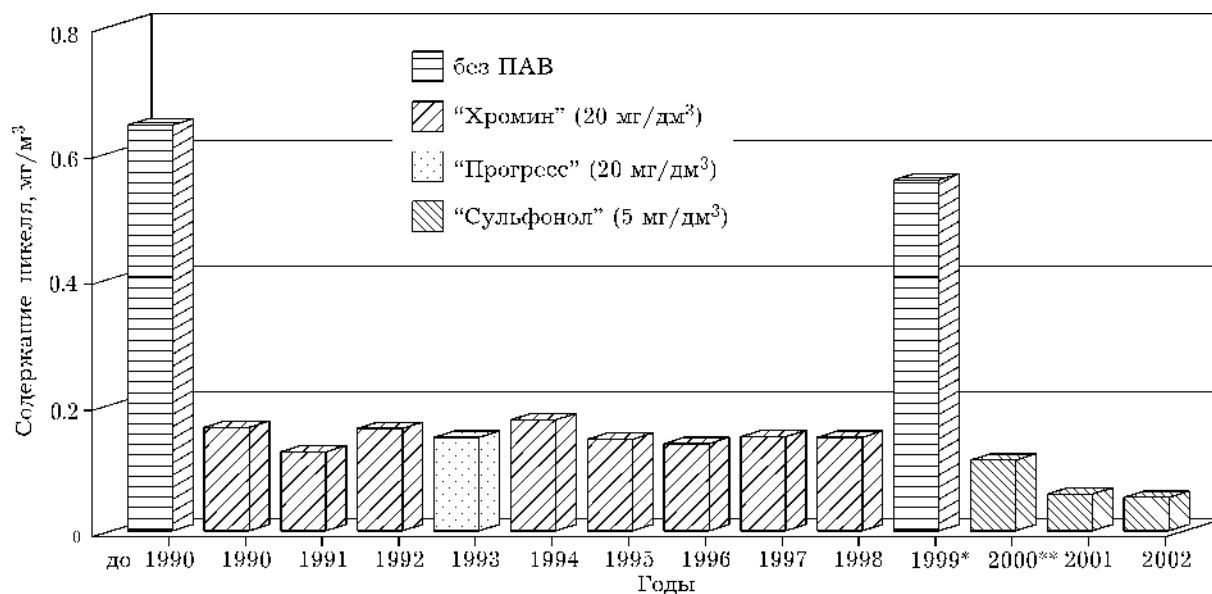


Fig. 3. Annual average content of nickel aerosols in AWS of NED according to Norilsk sanitary and epidemiologic agency during the time interval from 1985 to 2002.

*The use of the "Chromin" surfactant stopped in March, 1999.

**The use of the "Sulphonole" surfactant began in April, 2000.

fact that "Chromin" ceased to be used at the end of March, 1999, which affected the average annual content of aerosols. The twofold excess of nickel aerosol concentration in 2000 over the level of the next years is due to the same reason: "Sulphonole" has started to be used only since April, 2000.

Fluctuation of the aerosol content in 1990–1994 ($\approx 30\%$) is caused by the different annual rates of cathode nickel production and by the irregular supplies of "Chromin" in the economic situation of those years.

After one year of its use, the "Progress" surfactant was removed from the technological process owing to its high specific consumption caused by its significant decomposition in the process of electrolyte decontamination from iron and cobalt.

CONCLUSIONS

The given procedure for trial tests of surfactants is labour-saving and useful for selecting aerosol suppression surfactants having no adverse effects on the quality of cathode nickel for their potential use in nickel production.

More than 50 various surfactants have been tested by this procedure, and only 7 % of these met all the requirements and appeared to be applicable to nickel electrorefining processes.

The "Chromin", «Progress», and "Sulphonole" surfactants have passed pilot test; they

showed satisfactory results and were accepted for production of cathode nickel at "Norilsk Nickel" integrated iron and steel works.

The presently applied "Sulphonole" surfactant allows the concentration of nickel aerosols in the AWS of NED to be maintained at a level of 10 MPC ($\approx 0.05 \text{ mg/m}^3$).

REFERENCES

- 1 GOST 12.1.005–88, Sistema standartov bezopasnosti truda. Obshchiye sanitarno-gigienicheskiye trebovaniya k vozdukhу rabochey zony.
- 2 Tekhnologiya elektroliticheskogo rafinirovaniya nikelya za rubezhom, in M. L. Veisager and T. N. Meshkova (Eds.), Izd-vo TsNIITsVETMET, Moscow, 1991.
- 3 Poverkhnostno-aktivnye veshchestva i moyushchiye sredstva: Handbook, in A. A. Abramzon (Ed.), Giperoks, Moscow, 1993.
- 4 Poverkhnostno-aktivnye veshchestva i kompozitsii: Handbook, in M. Yu. Pletnev (Ed.), Firma Klavel, Moscow, 2002.
- 5 V. A. Petrosyan, L. G. Feoktistov, Organicheskaya elektrokimiya, vol. 2, Mir, Moscow, 1988.
- 6 Ya. F. Mezheny, Laboratorny praktikum po fizicheskoy i kolloidnoy khimii, GISL, Moscow, 1959, p. 327.
- 7 A. I. Levin, A. V. Pomosov, Laboratorny praktikum po teoreticheskoy elektrokhemii, Metallurgiya, Moscow, 1979, p. 312.
- 8 I. I. Lantseva, V. L. Kubasov, *Tsvet. metallurgiya*, 5 (1995) 19.
- 9 A. A. Nemodruk, N. V. Egiazarova *et al.*, Fotometricheskiye metody analiza v tsvetnoy metallurgii, Metallurgiya, Moscow, 1981, p. 90.
- 10 I. I. Lantseva, V. L. Kubasov, *Tsvet. metally*, 2 (1997) 27.
- 11 A. A. Abramzon, Poverkhnostno-aktivnye veshchestva, Khimiya, Leningrad, 1981.