

Appendix 15. Report by ICFSS on the 'Blind' test of the CIP

REPORT

on the decoding results of three test samples

Moscow July, 2007

As part of ENFSI-supervised international validation of **“The Complex Identification Procedure for determination of the nature and source of origin of products produced by mining and metallurgical operations and containing precious metals”** (further referred to as CIP), three test samples have been analyzed by the FSS Criminalistics Institute of Russia.

The main objective of the test examination: experimental demonstration of the CIP potential in detection and diagnostics of the products produced by OJSC MMC Norilsk Nickel (further referred to as Norilsk Nickel) in their mixes with each other and with American and South African materials containing platinum group metals (PGM).

Under testing requirements, three mixed test samples are to be presented for the analysis, and these samples should contain no more than two of Norilsk Nickel’s products, i.e. none, one or two. They can be mixtures of Norilsk Nickel’s own products or mixtures of Norilsk Nickel’s products with any PGM-bearing materials produced in SAR or America. Concentration of Norilsk Nickel product in the sample should be no less than 10 mass%.

Test samples were prepared by the SAPS Forensic Laboratory, an expert organization well experienced in handling PGM-bearing products of mineral processing. To prepare these samples, ten most frequently stolen Norilsk Nickel products were sent to the South Africa together with one sample of converter matte produced by Stillwater Mining company (this matte should be identified if present in the test sample). All samples are listed in Table 1. Russian samples were not analyzed before shipping to the South Africa: the information on their composition was taken from the data bank (RDB), which is an integral part of the CIP. American sample was analyzed before shipment in accordance with the CIP.

Three 30-grams test samples were received from Norilsk Nickel by the Russian FSS Criminalistics Institute. The samples were labeled **1**, **2** and **3**. The test target was to identify Norilsk Nickel products in the composition of the received samples.

Table 1.

№	RDB Code	Product
1	N18	Nickel sludge from Norilsk Nickel Polar Branch
2	N19	Copper sludge from Norilsk Nickel Polar Branch
3	N22	Calcined copper sludge cake From Norilsk Nickel Polar Branch
4	N23	Calcined nickel sludge cake from Norilsk Nickel Polar Branch
5	N24	Secondary anodes from Norilsk Nickel Polar Branch
6	N25	Washed cake after copper sponge leaching from Norilsk Nickel Polar Branch
7	N27	Slag anodes from Norilsk Nickel Polar Branch
8	N35	Leached secondary sludge from Norilsk Nickel Polar Branch
9	N37	Secondary sludge before leaching and washing from Norilsk Nickel Polar Branch
10	N38	Copper sponge before leaching and washing from Norilsk Nickel Polar Branch
11	SMC1	Converter matte From Stillwater Mining Company

STUDY DESCRIPTION

The received samples were analyzed in accordance with “**The Complex Identification Procedure for determination of the nature and source of origin of products produced by mining and metallurgical operations and containing precious metals**”.

The first stage of the study involved the determination of the samples’ integral element composition by Scanning Electron Microscopy/Electron Probe X-ray Microanalysis (SEM/EPMA) method. The results obtained were used for initial diagnostics of substances, and in the selection of sample preparation method for further analysis. The results are presented in Figures 1-3.

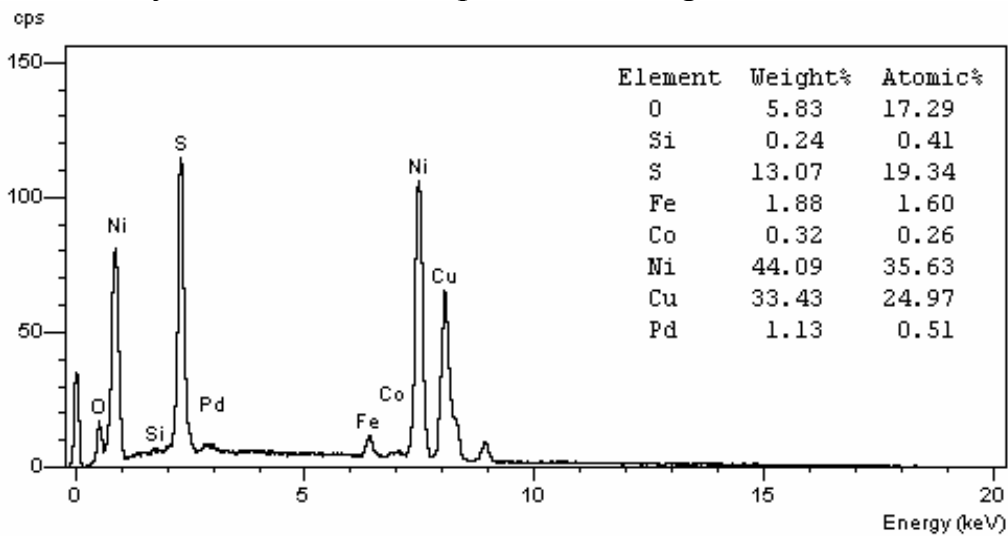


Fig. 1. Integral element composition of the test sample 1.

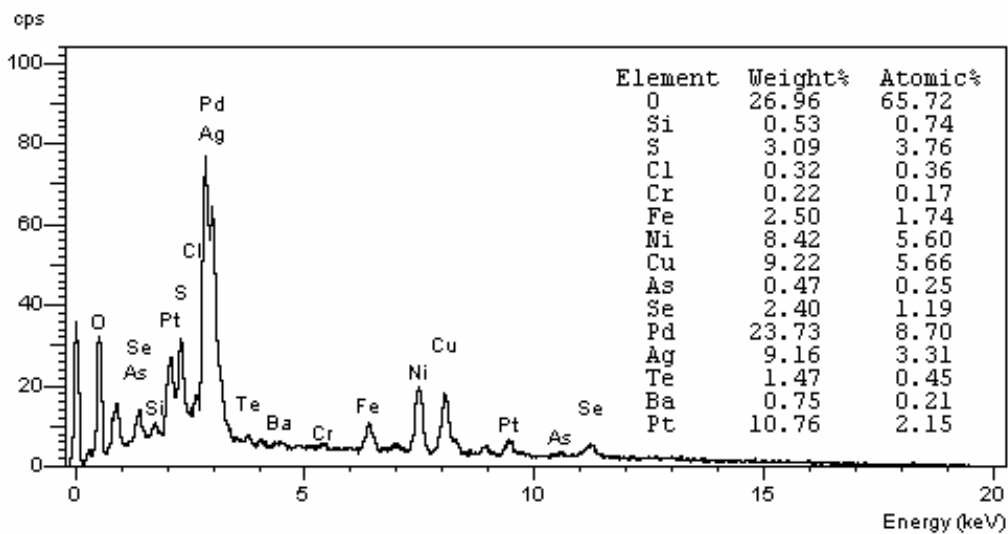


Fig. 2. Integral element composition of the test sample 2.

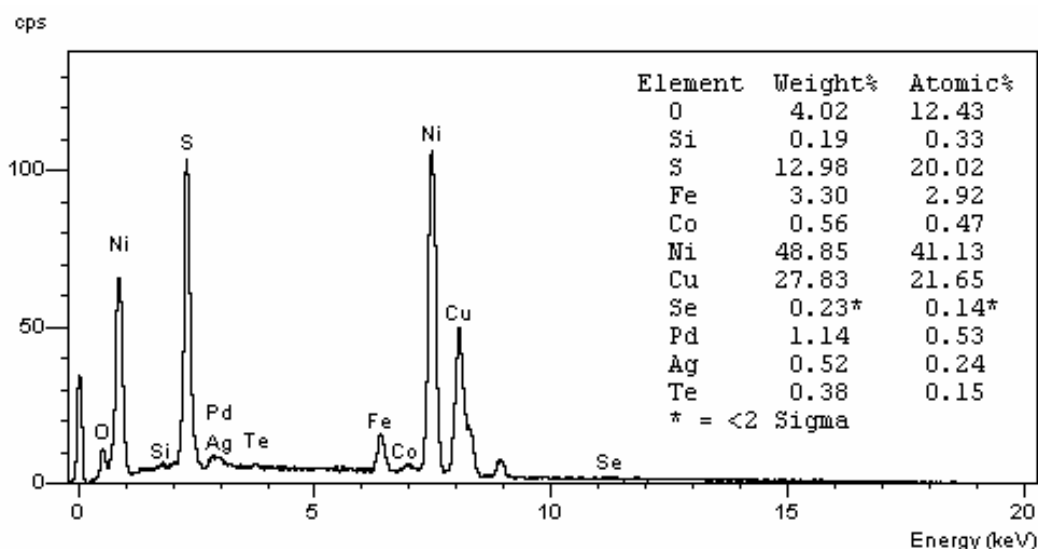


Fig. 3. Integral element composition of the test sample 3.

Based on the results of the first stage, it may be established that all three test samples are made of materials which are the products of copper-nickel sulphide ore processing. Test sample 2 primarily consists of concentrated product (products) with some PGM amount.

The results of bulk element composition analysis are summarized in Table 2. The analysis was carried out using the methods of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Table 2.

Element	Element weight percentage, %		
	1	2	3
Nickel	44,3	8,35	49,1
Copper	27,6	8,78	14,61
Gold	0,0139	1,59	0,342
Silver	0,0175	10,5	3,05
Platinum	0,381	6,49	1,77
Palladium	0,59	24,8	5,49
Rhodium	0,098	0,188	0,185
Ruthenium	0,043	0,057	0,068
Iridium	0,028	0,079	0,035
Cobalt	0,40	0,30	1,10
Iron	0,94	2,72	7,77
Sulfur	20,3	3,44	8,12
Selenium	0,071	3,60	0,71
Tellurium	0,027	1,51	0,60
Arsenic	0,027	0,54	0,44

Element	Element weight percentage, %		
	1	2	3
Lead	0,117	1,75	0,498
Tin	0,0012	0,58	0,082
Antimony	<0,0001	0,32	0,063
Barium	0,0001	0,83	0,0017
Chrome	0,0027	0,128	0,007
Manganese	0,0005	0,003	0,0010
Titanium	0,002	0,029	0,002
Tungsten	<0,0001	0,0009	<0,0001
Molybdenum	0,0014	0,0009	0,0034
Sodium	0,0131	0,0150	0,0102
Potassium	0,001	0,0064	0,0016
Calcium	0,128	0,170	0,123
Magnesium	0,004	0,061	0,005
Aluminum	0,002	0,011	0,009
Phosphorus	0,0195	0,050	0,0080

The samples' phase compositions determined by X-Ray Diffractometry (XRD) method are as follows:

Sample 1. Phase composition of the sample is represented by Nickel Sulphide Ni_3S_2 , Copper Sulphides $Cu_{2-x}S$ and Cu_2S , and possibly by the solid solution of Ni or Fe type. The diffractogram for this sample is shown in Fig. 4.

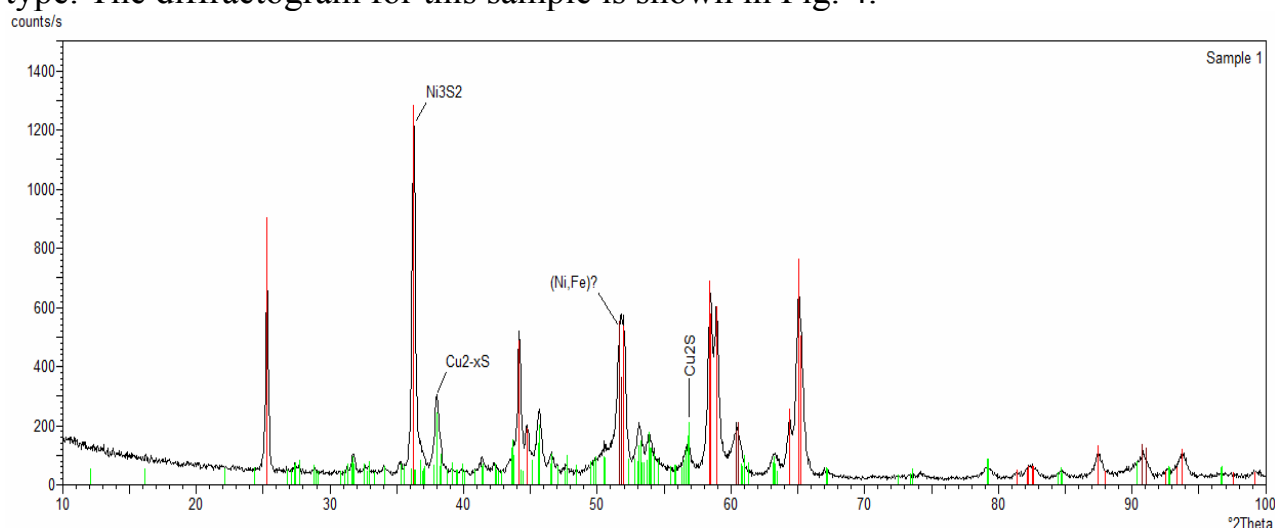


Fig. 4. Sample 1 Diffractogram

Sample 2. Phase composition of the sample is represented by solid solution of the type (Pt, Pd); metal oxides Fe_2O_3 and/or Fe_3O_4 , $(Ni,Cu)O$ and/or NiO ; Copper Sulphide $Cu_{2-x}S$, Silver Chloride $AgCl$; Barium Sulphide $BaSO_4$; Copper Hydro-oxi-

sulphate $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ and Silicium dioxide SiO_2 . The diffractogram of this sample is shown in Fig. 5.

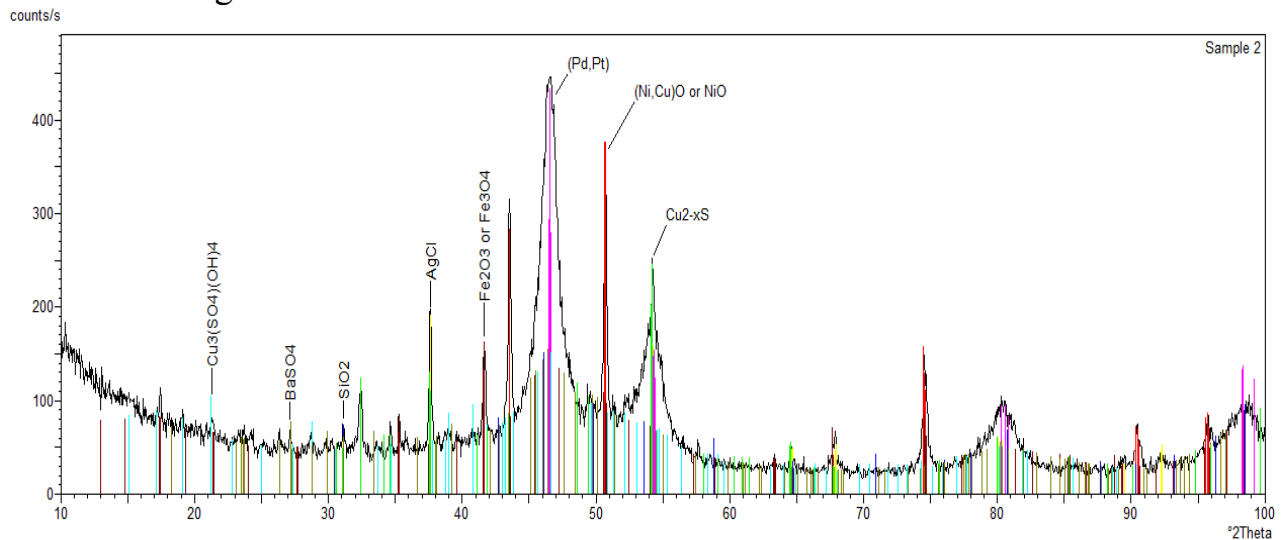


Fig. 5. Sample 2 Diffractogram

Sample 3. Phase composition of this sample is represented by metal Sulphide Ni_3S_2 , Cu_{2-x}S , Cu_2S , Cu_5FeS_4 and solid solution of the type (Ni, Fe). The diffractogram of this sample is shown in Fig. 6.

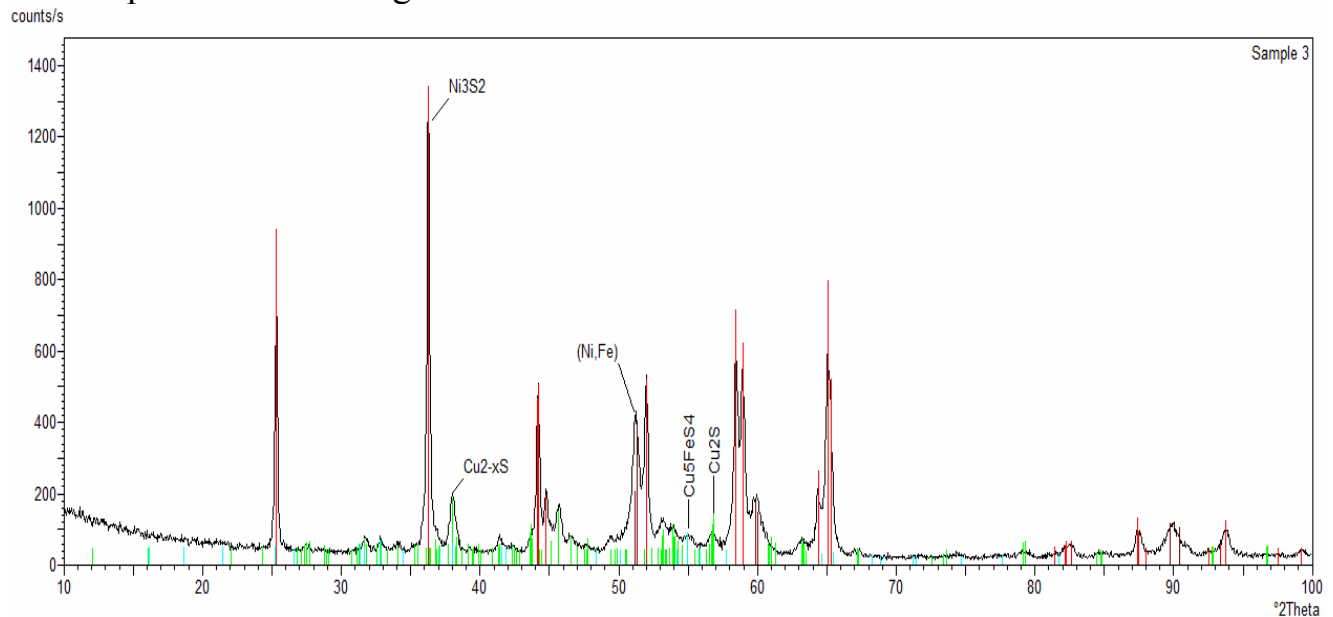


Fig. 6. Sample 3 Diffractogram

Using a method of direct superposition of the analyzed samples diffractograms on the diffractograms of processed ore products containing precious metals and presented in the RDB (“fingerprints method”), the following was established:

Sample 1. Sample 1 diffractogram demonstrates best match with the diffractogram of sample SMC1 and similar to each other diffractograms of the converter matte samples analyzed in the Institute in 2003 and produced by one of the South African companies (e.g., Impala Platinum and Lonmin Platinum). (For further convenience the last type

of samples shall be referred to as CM SAR).

Superposition of the aforementioned samples' diffractograms is shown in Fig. 7.

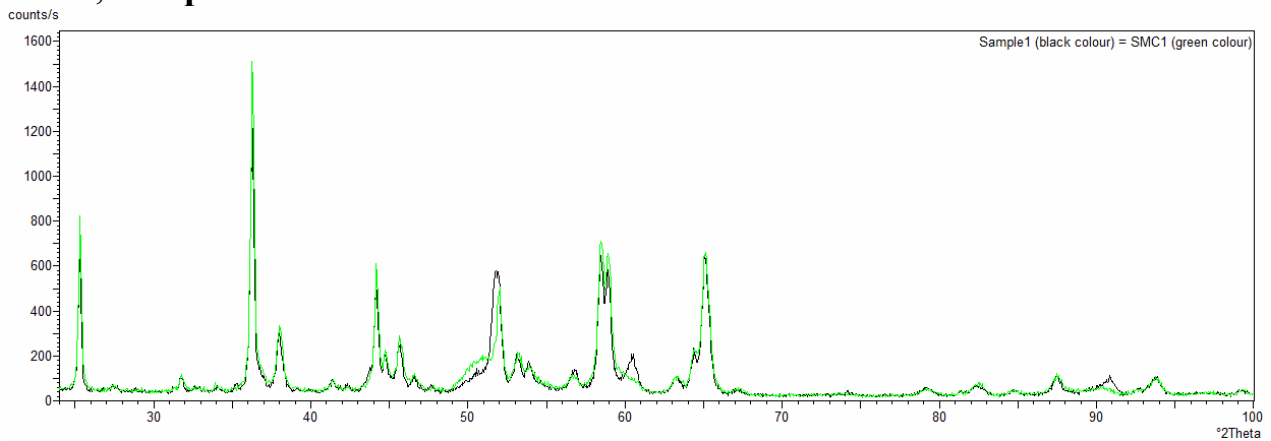
Thus, **Sample 1 = SMC1 + CM SAR**

Sample 2. Sample 2 diffractogram demonstrates best match with the diffractogram of samples N23 (calcined nickel sludge cake), N35 (Secondary leached sludge) or N37 (secondary sludge before leaching and washing). Superposition of these diffractograms is shown in Fig. 8. XRD method does not allow determining which of the samples N35 or N37 is present in test sample 2.

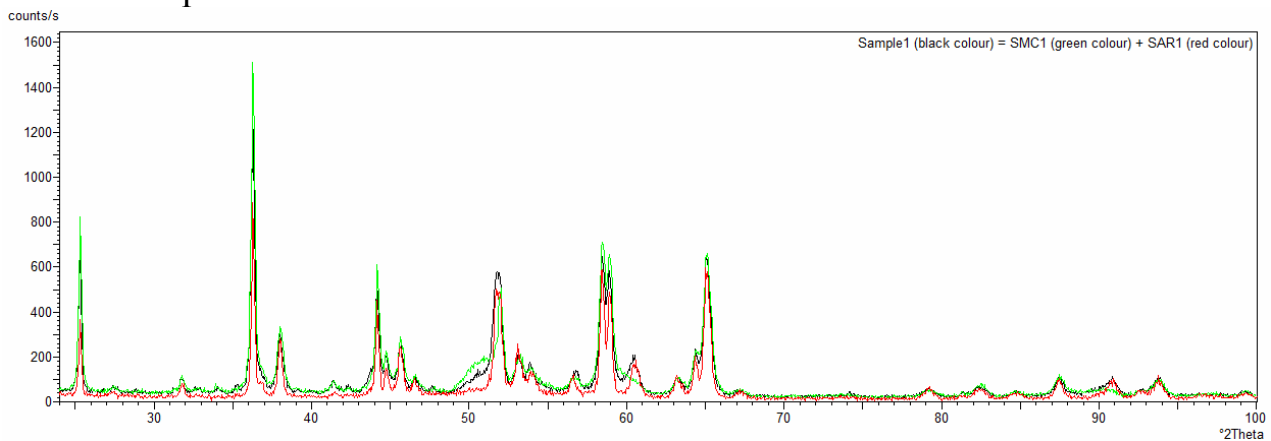
Thus, **Sample 2 = N35 or N37 + N23.**

Sample 3. Sample 3 diffractogram demonstrates best match with the diffractograms of samples SMC1, CM SAR, N24 (secondary anodes) or N27 (slag anodes). Superposition of these diffractograms is shown in Fig. 9. XRD method does not allow determining which of the samples N24 or N27 is present in test sample 3.

Thus, **Sample 3 = SMC1 + CM SAR + N24 or N27.**

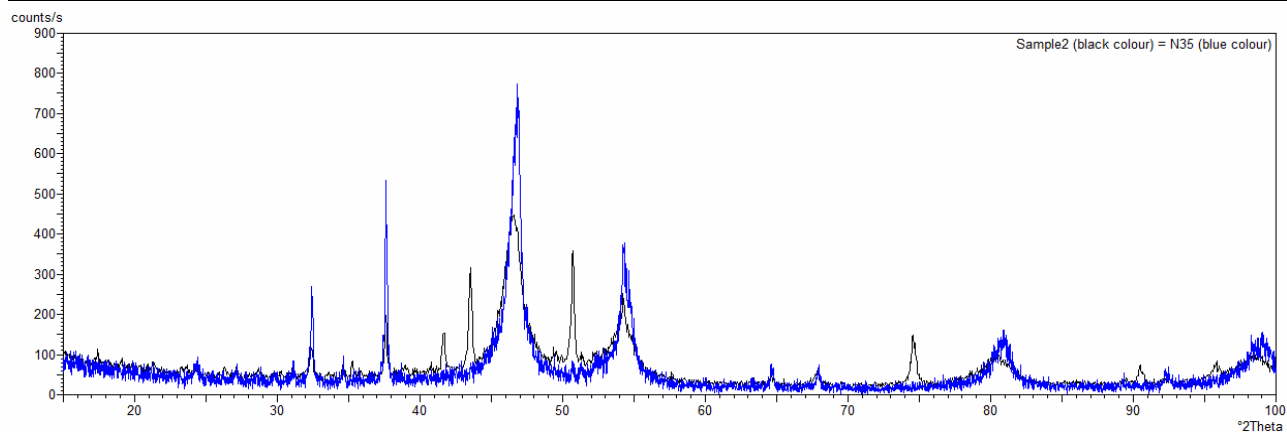


a. Sample 1 and SMC1.

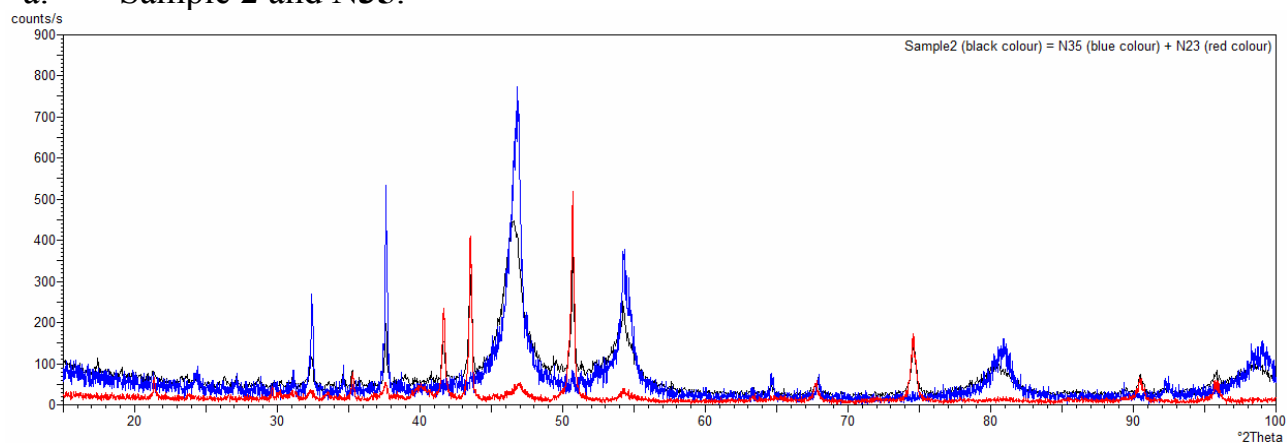


b. Sample 1, SMC1 and CM SAR

Fig. 7. Superposition of Sample 1, SMC1 and CM SAR diffractograms.

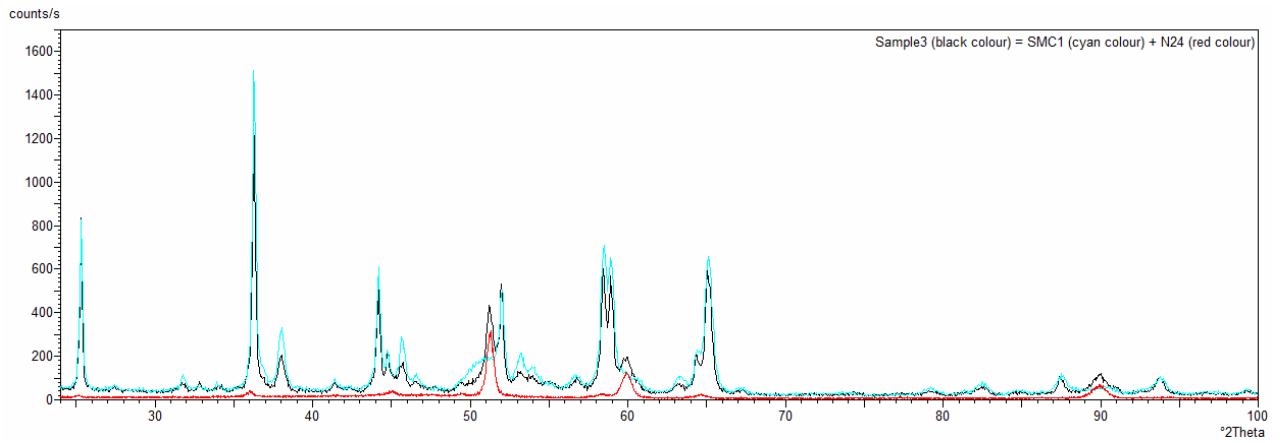


a. Sample 2 and N35.

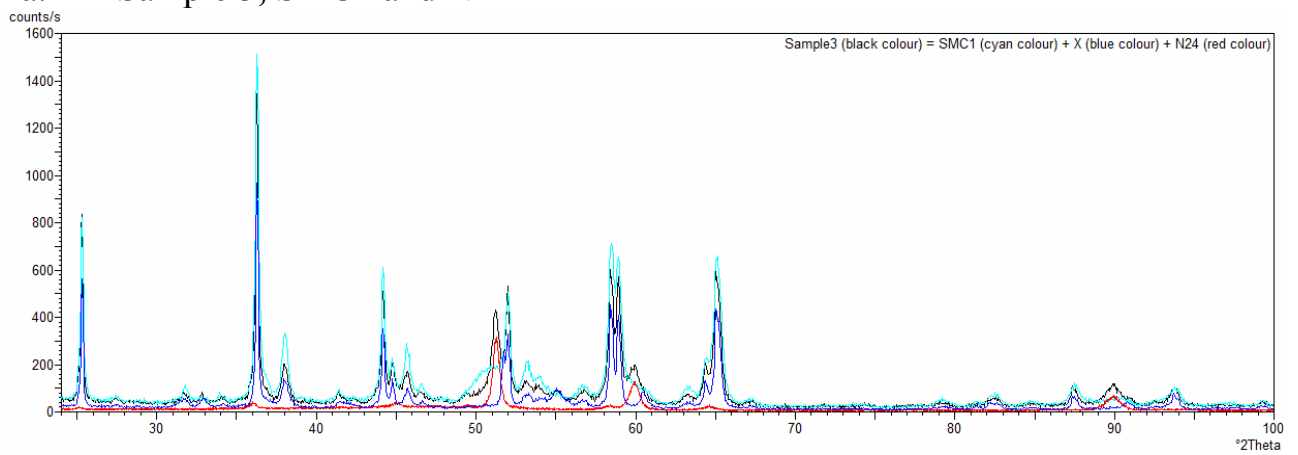


b. Sample 2, N35 and N23

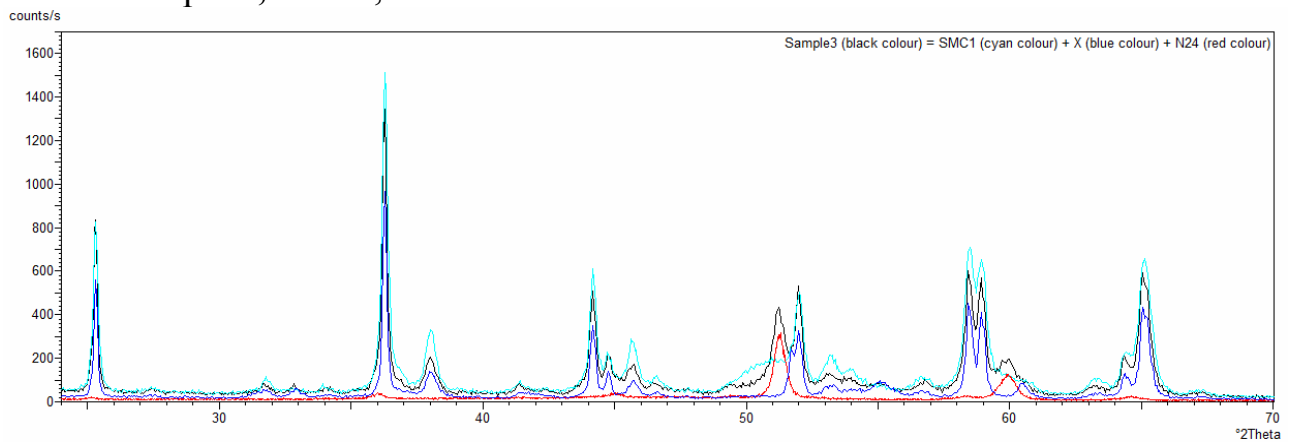
Fig. 8. Superposition of Sample 2, N35 and N23 diffractograms.



a. Sample 3, SMC1 and N24



b. Sample 3, SMC1, CM SAR and N24



c. Sample 3, SMC1, CM SAR and N24 (magnified)

Fig. 9. Superposition of Sample 3, SMC1, CM SAR and N24 diffractograms.

At the last stage, the analysis of micro particles that form the material mixed test samples was carried out.

Analytical results show that the material of samples **1** and **3** is mainly formed by micro particles and their aggregates that represent copper and nickel sulphides with traces of precious metals (Pd, Pt). Sample 2 is primarily formed by micro particles that represent a solid solution of precious metals, mainly Palladium and some other characteristic elements (Te, Se and others).

Sample 1.

The following types of micro particles have been detected in the material of Sample 1. Typical spectra of these micro particles are shown in Fig. 10.

Ni-Cu-S-(Fe);

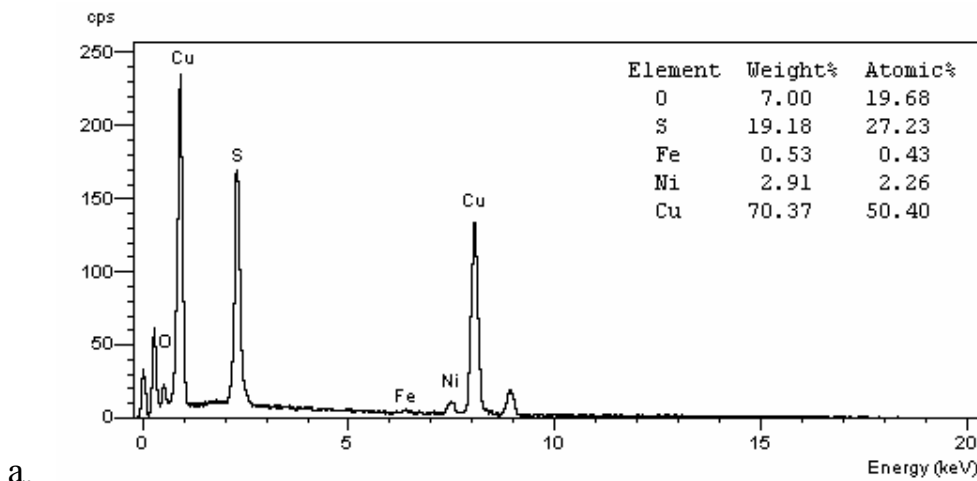
Cu-Ni-S-(Fe);

Ni-Cu-S-Pd-(Fe)-(Co);

Cu-Ni-S-Pd-(Fe)-(Co);

Pt-Ni-Cu-S-Pd-(Fe)-(Co).

Correlation of analytical picks' intensities of energy dispersion spectra and element compositions of detected micro particles are typical for Stillwater Mining's converter matte (sample SMC1). The ratio of micro particles of the last three types in the material of this sample also corresponds to sample SMC1. Overbalance of the first two types of microparticles is observed, what in accordance with data of the phase analysis can be explained by the presence of a converter matte type CM SAR.



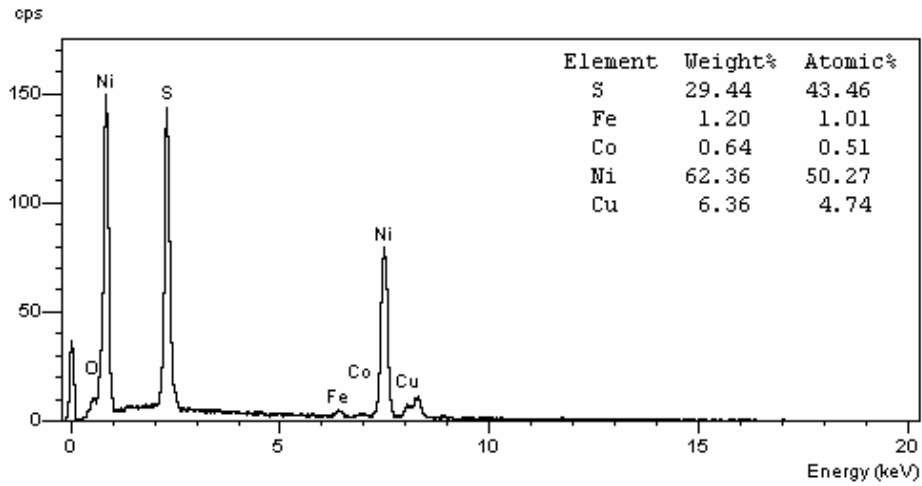
a.

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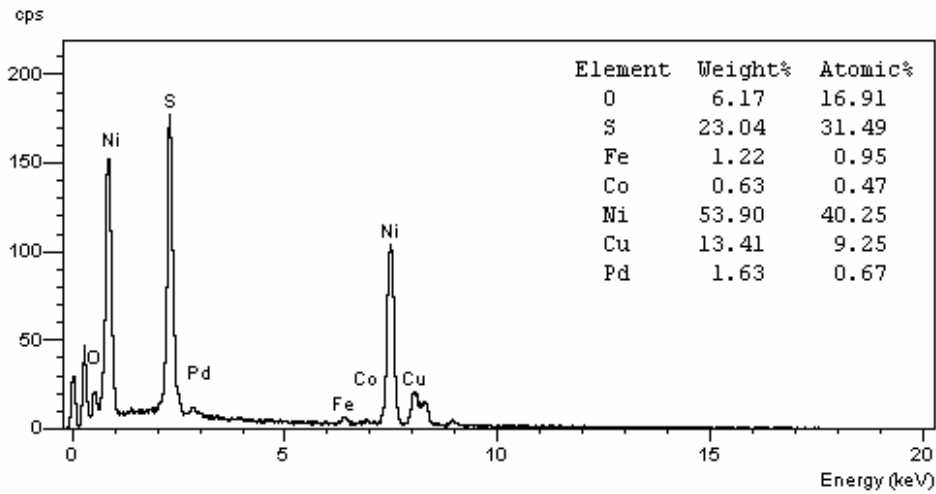
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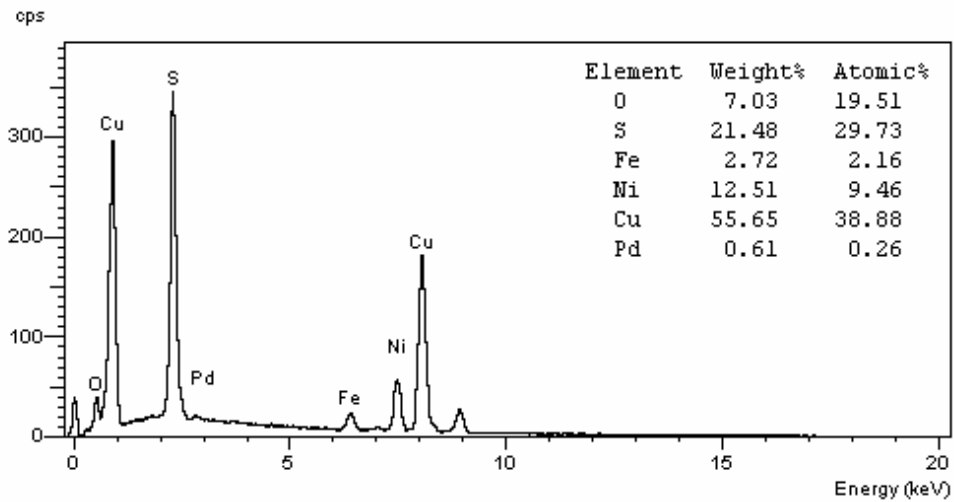
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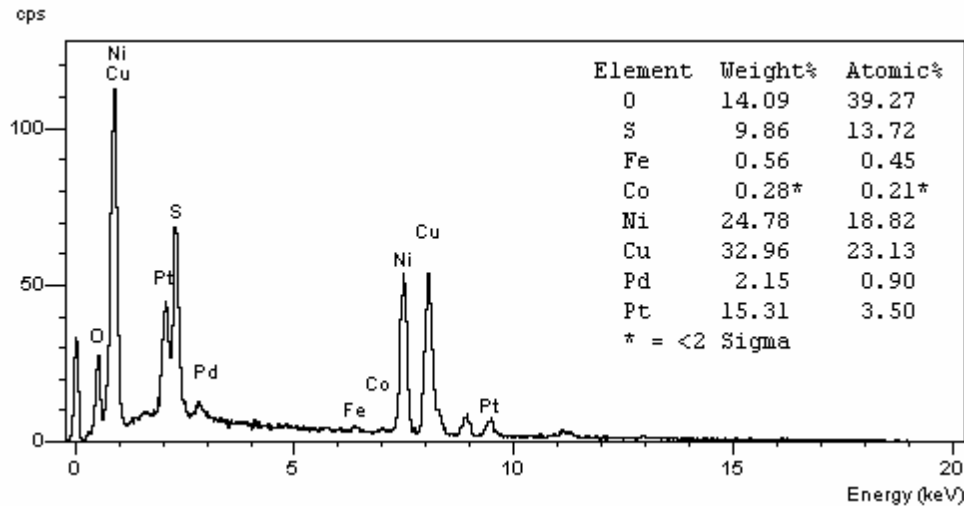
b.



c.



d.



e.

Figure 10. Test sample 1 microparticles characteristic spectra.

- a. Type **Ni-Cu-S-(Fe)**;
- b. Type **Cu-Ni-S-(Fe)**;
- c. Type **Ni-Cu-S-Pd-(Fe)-(Co)**;
- d. Type **Cu-Ni-S-Pd-(Fe)-(Co)**;
- e. Type **Pt-Ni-Cu-S-Pd-(Fe)-(Co)**.

Thus, the analytical results show that material of test sample 1 consists of Stillwater Mining Company's converter matte (sample SVC1) and converter mate of the type CV SAR.

Evaluation of Stillwater matte content (sample SVC1) in Sample 1 was done by comparing the information on bulk element compositions (Table 3). Palladium concentration was taken as benchmark in this evaluation. Estimated content of SMC1 matte approximately amounted to 50 mass%.

Table 3.

Bulk element compositions of sample 1 and its ingredients

Elements	Sample 1	SMC1 Converter matte	CM SAR Converter matte
Ni	44.3000	44.1000	42.4600
Cu	27.6000	28.2000	25.6500
Au	0.0139	0.0208	0.0120
Ag	0.0175	0.0263	0.0083
Pt	0.3810	0.8000	0.1655
Pd	0.5900	1.2100	0.1005
Rh	0.0980	0.0688	0.0219
Ru	0.0430	0.0036	0.0380
Ir	0.0280	0.0014	0.0276
Co	0.4000	0.4480	0.3395
Fe	0.9400	2.0700	3.5600
S	20.3000	22.1000	20.9000
Se	0.0710	0.0710	0.0615
Te	0.0270	0.0500	0.0197
As	0.0270	0.0250	0.0302

Elements	Sample 1	SMC1 Converter matte	CM SAR Converter matte
Pb	0.1170	0.2030	0.1240
Sn	0.0012	0.0097	0.0046
Sb	<0,0001	<0,0001	<0,0001
Ba	0.0001	0.0053	0.0001
Cr	0.0027	0.0100	0.0010
Mn	0.0005	0.0100	0.0010
Ti	0.0020	0.0100	0.0018
Na	0.0131	0.0816	0.0003
K	0.0010	0.0115	0.0003
Ca	0.1280	0.1072	0.0061
Mg	0.0040	0.0163	0.0012
Al	0.0020	0.0355	0.0062
P	0.0195	0.0200	<0,001

Sample 3.

The particles that form the material of this sample greatly vary by their size (fine and coarse fractions). Fine particles are identical by their element composition to the particles present in test sample 1. Quantitative ratio of particles of each type present in the fine fraction also corresponds to sample 1. It means that test sample 3 contains Stillwater matte (sample SMC1) and the matte of CM SAR type.

As for their size, morphology and composition, coarse fraction particles are similar to those of secondary anodes produced by Norilsk Nickel Polar Branch (N24). Typical spectrum of coarse particles is shown in Fig. 11.

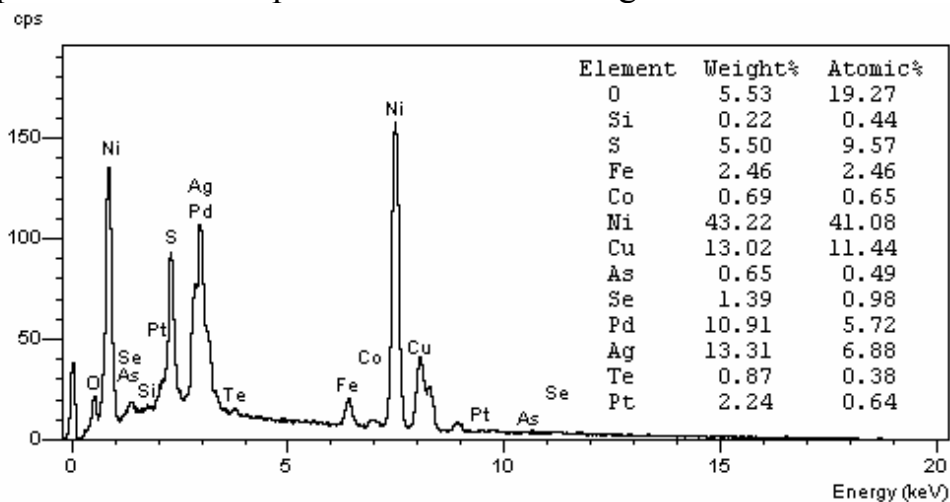


Fig. 11. Typical spectrum of coarse particles in sample 3

The coarse fraction ratio in mixture No. 3 was determined by gravimetric method, using a set of screens and RC 2108 analytical scales with 0.01 mg weight resolution (manufacturer – Sartorius AG, Germany). Fraction were classified using screens with mesh dimension 0.315, 0.16 and 0.1 mm. Particles collected from each of the screens

were thoroughly washed with alcohol, dried and weighed. Their element composition was determined after that using EPMA method. It was established that all particles retained on these screens (mesh size 0.315 mm, 0.16 mm, 0.1 mm) were similar by their composition to the particles present in secondary anodes. Based on weighting results it was established that the ratio of these particles in mixture No.3 is 59.6%.

Pictures of the coarse fraction particles from test sample No.3 and secondary anodes particles are shown in Fig. 12.

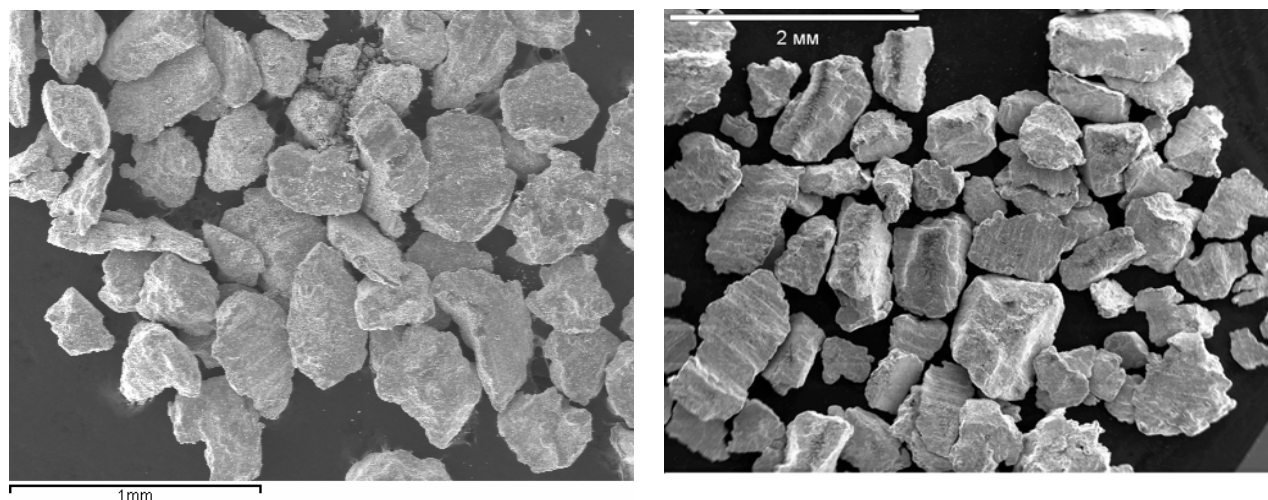


Fig. 12. Coarse fraction particles from test sample No.3 (a) and secondary anodes particles (b).

In addition, bulk element composition of the coarse fraction in sample 3 was determined using ICP-OES and ICP-MS methods. The results are given in Table 4.

Table 4.

Bulk element composition of sample 3 and its ingredients

	Sample 3	SMC1 Converter matte	CM SAR Converter matte	Secondary anodes N24	Sample 3 coarse fraction
Ni	49.1	44.1	42.46	53.61	55.4
Cu	14.6	28.2	25.65	9.72	7.36
Au	0.342	0.0208	0.012	0.497	0.673
Ag	3.05	0.0263	0.0083	4.11	6.05
Pt	1.77	0.8	0.1655	2.33	2.63
Pd	5.49	1.21	0.1005	8.63	9.06
Rh	0.185	0.0688	0.0219	0.2133	0.237
Ru	0.068	0.0036	0.0380	0.2649	0.0848
Ir	0.035	0.0014	0.0276	0.0489	0.038
Co	1.1	0.448	0.3395	1.63	1.16
Fe	7.77	2.07	3.56	10.92	5.45

	Sample 3	SMC1 Converter matte	CM SAR Converter matte	Secondary anodes N24	Sample 3 coarse fraction
S	8.12	22.1	20.9	1.72	1.61
Se	0.71	0.071	0.0615	0.5391	0.825
Te	0.6	0.05	0.0197	0.8627	0.783
As	0.44	0.025	0.03015	0.7221	0.367
Pb	0.498	0.203	0.124	0.6164	0.741
Sn	0.082	0.0097	0.0046	0.4523	0.154
Sb	0.063	<0,0001	<0,0001	0.2519	0.149
Ba	0.0017	0.0053	0.0001	0.0030	0.0003
Cr	0.007	0.01	0.001	0.0292	<0,0001
Mn	0.001	0.01	0.0010	0.0017	0.0008
Ti	0.002	0.01	0.0018	0.0013	0.0005
Na	0.0102	0.0816	0.0003	0.0938	<0,0001
K	0.0016	0.0115	0.0003	0.0167	0.0047
Ca	0.123	0.1072	0.0061	0.0076	0.0151
Mg	0.005	0.0163	0.0012	0.0048	0.0006
Al	0.009	0.0355	0.0062	0.0032	0.0047
P	0.008	0.02	<0,001	0.0051	0.0046

Thus a conclusion can be made that material of test sample **3** contains: **secondary anodes (N24)** from Norilsk Nickel Polar Branch - 60 weigh %; Stillwater Mining Company **converter matte (SMC1)** and **converter matte of CM SAR type** - about 20 mass% each.

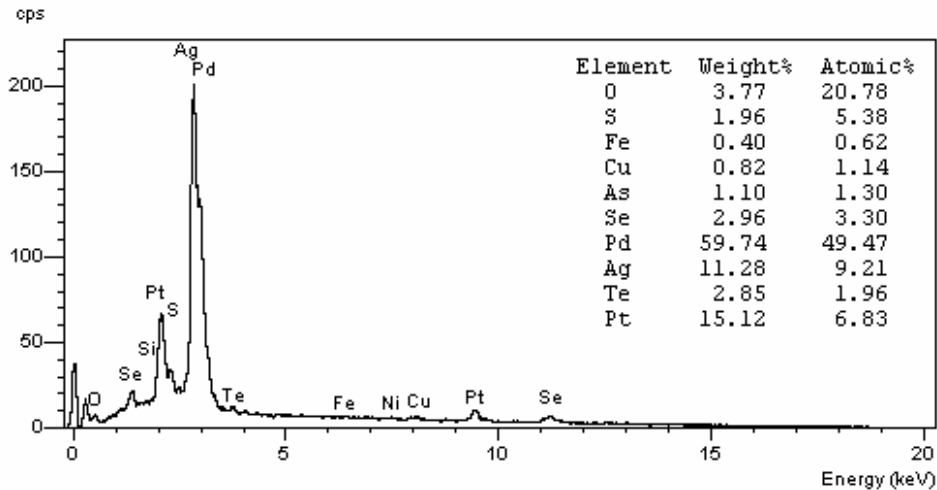
Sample 2.

The following types of microparticles have been detected in the material of Sample **2** (for further convenience types will be numerated).

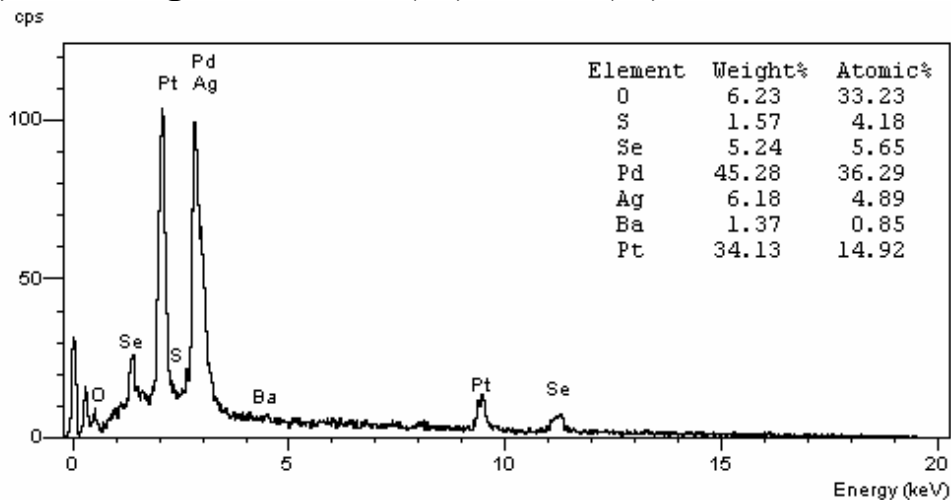
- 1) **Pd–Ag–Pt–(O)–As–Se–(Si)–(Au)–S–(Pb)–(Cl)–Te–(Fe)–(Ni)–Cu;**
- 2) **Pt–Pd–Ag–O–As–Se–S–(Pb)–Te–Fe–(Ni)–Cu;**
- 3) **Pb–O–(As)–(Se)–(Pt)–Pd–Ag–(Te)–(Fe)–(Ni)–(Cu);**
- 4) **Pd–Ag–Pt–Sn–(Sb)–O–As–Se–(Si)–(Au)–S–Pb–(Te)–Fe–(Ni)–Cu;**
- 5) **Ni–O–(As)–(Se)–(Si)–(Pt)–(S)–(Pb)–(Pd)–(Ag)–(Fe)–(Co)–(Cu);**
- 6) **Ni–Cu–Fe–(Co)–Pd–(Ag)–Pt–(Au)–Te–(As)–(Se)–(Ba)–(Cr)–(Pb)–O–S–Si–(Ca);**
- 7) **Ni–Cu–Fe–(Co)–Pd–(Ag)–(Te)–(As)–(Cr)–O–S–Si;**
- 8) **Cu–Ni–Se–Ag–(Pt)–S–O–(As)–(Si)–(Cl)–Pd–Te–(Ba)–(Fe);**
- 9) **Se–Ag–O–(As)–(Si)–(Pt)–S–(Cl)–(Pd)–Te–(Ba)–(Fe)–(Ni)–Cu;**
- 10) **Ba–S–O–(Se)–(Pd)–(Ag)–(Te)–(Ni)–(Cu).**

Based on the ratio of analytical picks' intensities in the energy dispersion spectra, on element composition and quantitative ratio of particles of each type, the particles listed as 1) – 5) are typical for **leached secondary sludge** from Norilsk Nickel Polar Branch (N35). The fifth type is represented by nickel oxide micro particles. Typical spectra for the first four types oare presented in Fig. 13.

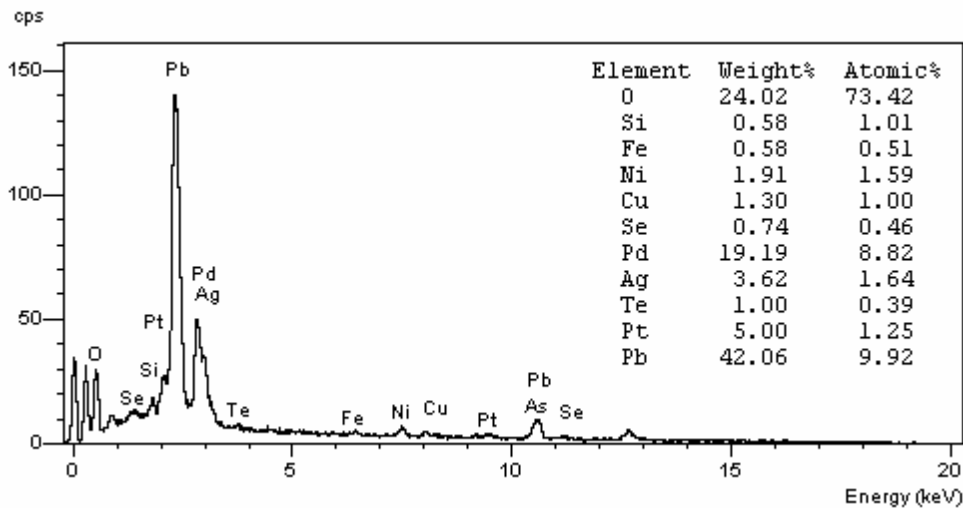
1) Pd–Ag–Pt–(O)–As–Se–(Si)–(Au)–S–(Pb)–(Cl)–Te–(Fe)–(Ni)–Cu



2) Pt–Pd–Ag–O–As–Se–S–(Pb)–Te–Fe–(Ni)–Cu;



3) Pb–O–(As)–(Se)–(Pt)–Pd–Ag–(Te)–(Fe)–(Ni)–(Cu)



4) Pd–Ag–Pt–Sn–(Sb)–O–As–Se–(Si)–(Au)–S–Pb–(Te)–Fe–(Ni)–Cu

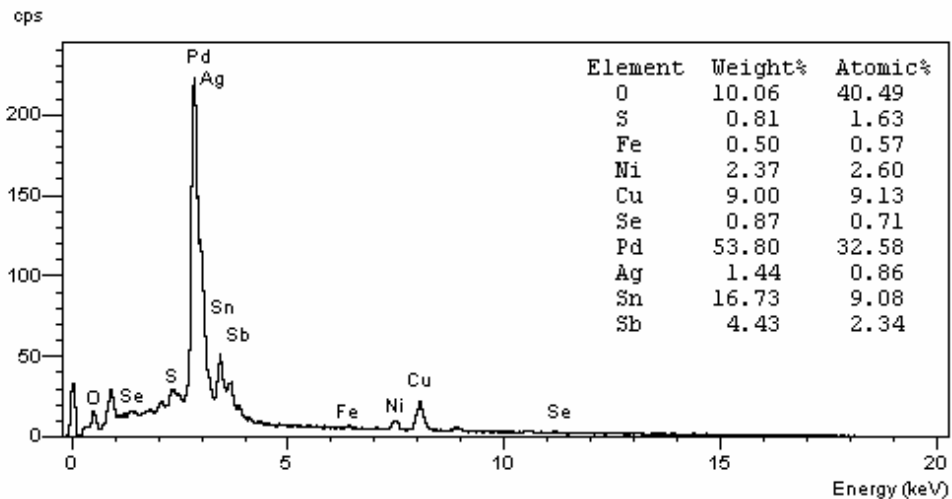
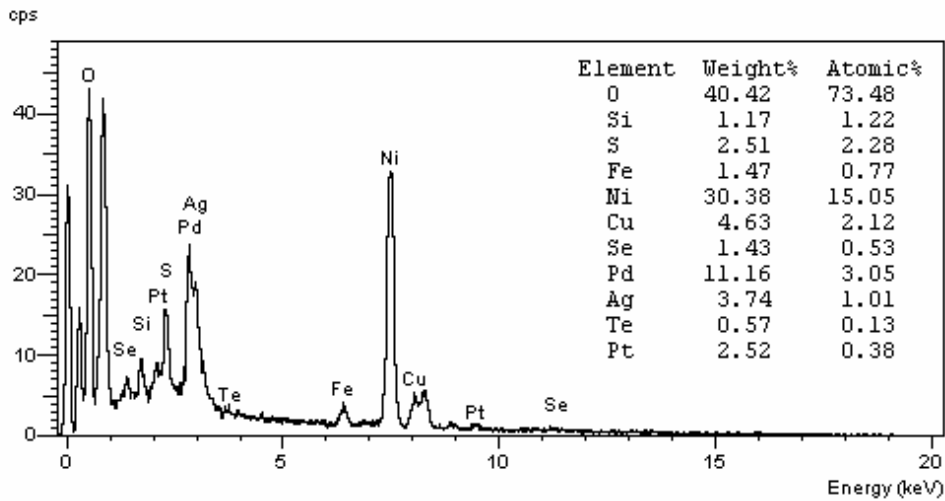


Fig. 13. Typical spectra of Sample 2 micro particles (types 1-4).

Micro particles of types 6 and 7 present in sample 2 and their ratio are typical for **calcined nickel sludge cake** from Norilsk Nickel Polar Branch (N23). Another characteristic feature of the product is the presence of particles with higher chrome content among micro particles of the 7th type. Typical spectra are shown in Fig. 14.

Particles of the next three types detected in the material of sample 2 are very similar to the particles of copper sludge produced by Norilsk Nickel Polar Branch (N19). There is, however, an important difference between these particles and copper sludge particles described in the data bank: sample 2 particles have higher Cu, S and O₂ contents, which may be probably explained by the presence of copper sulphates. Moreover, a major part of these particles contains platinum, whereas the ratio of Pt-bearing particles in Norilsk Nickel’s copper sludge doesn’t exceed 10%. Thus, a conclusion may be made that sample 2 contains material of unknown origin, but its composition is close to that of copper sludge produced by Norilsk Nickel Polar Branch.

6) Ni-Cu-Fe-(Co)-Pd-(Ag)-Pt-(Au)-Te-(As)-(Se)-(Ba)-(Cr)-(Pb)-O-S-Si-(Ca)



7) Ni-Cu-Fe-(Co)-Pd-(Ag)-(Te)-(As)-(Cr)-O-S-Si

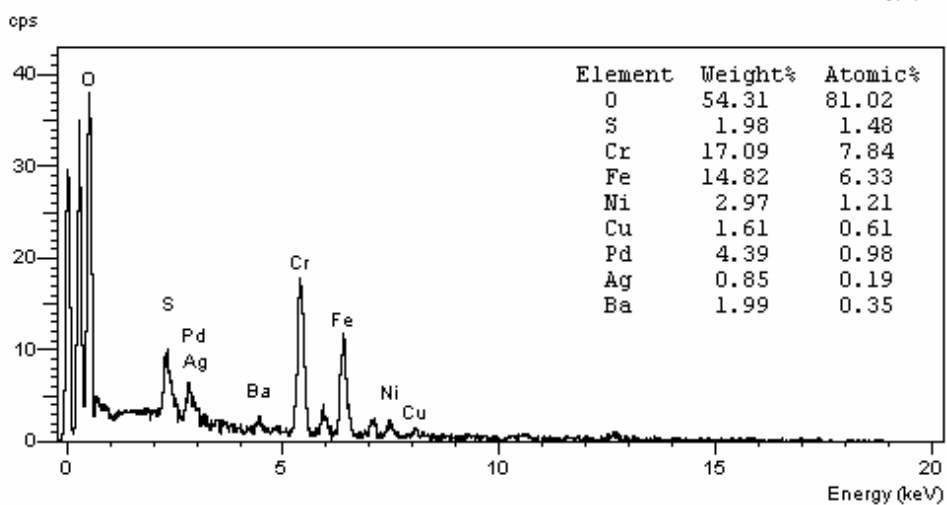
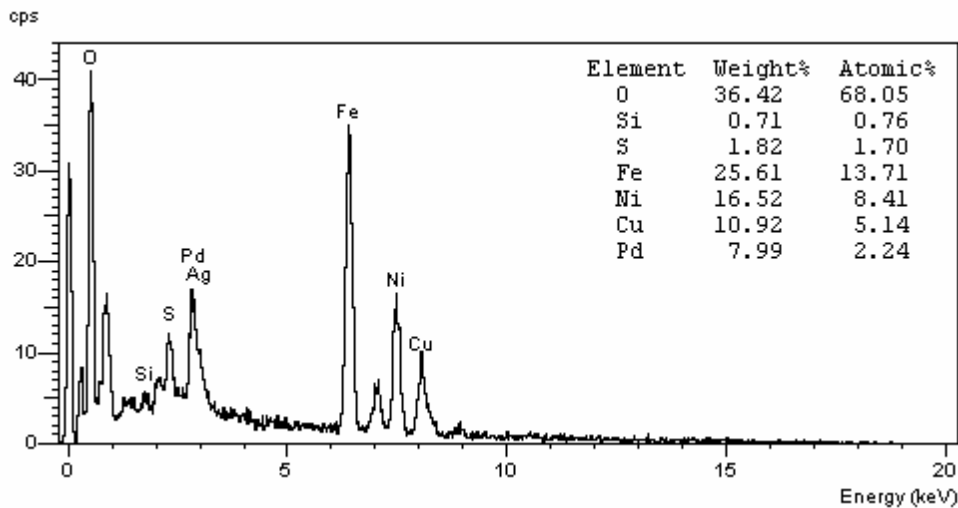


Fig. 14. Typical spectra of Sample 2 micro particles (types 6 and 7).

Microparticles of the next three types (8, 9 and 10) detected in the composition of sample 2 are characteristic for Copper slime (N19) from Norilsk Nickel Polar Branch. Under review there are some differences in material composition of given

microparticles and copper slime microparticles composition, presented in the data base. In particular there are the following differences: higher content of copper, sulfur and oxygen, and most likely these differences could be caused by the presence of deposition or dissemination of the copper sulphate in the microparticles composition.

Evaluation of the Leached secondary sludge (N35), Calcined nickel sludge cake (N23) and Copper sludge (N 19) from Norilsk Nickel Polar Branch content in the test sample 2 has been conducted basing on the comparison of bulk element composition data (see Table 5). For the *leached secondary sludge* evaluation has been done on the basis of Palladium concentration, for *calcined nickel sludge cake* – on the basis of Iron and Cobalt content. Leached secondary sludge (N35) content is about 50 mass%, calcined nickel sludge cake (N23) content is about 25 mass%, and the rest is the Copper sludge (N 19), its content is about 25 mass%.

Table 5.

Bulk element composition of sample 2 and its ingredients

	Sample 2	Calcined nickel sludge cake (N23)	Leached secondary sludge (N35)	Copper sludge (N 19)
Ni	8,35	27,38	0,66	14,74
Cu	8,78	6,55	2,48	28,39
Au	1,59	0,18	2,85	0,27
Ag	10,5	1,36	11,14	6,47
Pt	6,49	1,32	13,26	0,76
Pd	24,8	5,63	47,91	2,51
Rh	0,188	0,128	0,437	0,027
Ru	0,057	0,029	0,133	0,009
Ir	0,079	0,015	0,042	0,004
Co	0,3	1,231	0,017	0,043
Fe	2,72	12,03	0,33	0,29
S	3,44	2,02	0,92	3,89
Se	3,6	0,27	2,41	9,46
Te	1,51	0,48	2,63	1,43
As	0,54	0,55	2,06	0,20
Pb	1,75	0,40	2,49	0,20
Sn	0,58	0,12	2,05	0,00
Sb	0,32	0,07	1,14	0,01
Ba	0,83	0,636	0,049	2,54

Thus, a conclusion can be made that material of test sample 2 contains: **leached secondary sludge (N35), calcined nickel sludge cake (N23) and copper sludge (N19)** from Norilsk Nickel Polar Branch, in the content of about 50 mass%, 25 mass% and 25 mass%, respectively.

CONCLUSIONS

Upon the results of this comprehensive analysis the following conclusions can be made:

1. In the composition of **test sample 1, Stillwater Mining Company converter matte (SMC1)** is present in the quantity of about 50 mass%.
2. In the composition of **test sample 2, leached secondary sludge (N35), calcined nickel sludge cake (N23) and copper sludge (N19)** from Norilsk Nickel Polar Branch, in the content of about 50 mass%, 25 mass% and 25 mass%, respectively.
3. In the composition of **test sample 3, secondary anodes (N24)** from **Norilsk Nickel Polar Branch** is present in the quantity of about 60 mass% and **Stillwater Mining Company converter matte (SMC1)** is present in the quantity of about 20 mass%.

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