

Technological Capabilities of Hydrocarbonyl Processes in the Concentration and Separation of Platinum Group Metals

**I. V. Fedoseev[‡], Yu. A. Kotlyar[§],
V. V. Vasekin^{*}, N. V. Rovinskaya[¶]**

JSC R&PC Supermetal, Ozerkovskaya Nab.,
22/24, corp. 2, Moscow, 115184, Russia

*Email: [‡]prof.igor.fedoseev@gmail.com;

[§]amk512@mail.ru;

*vasekin@supermetal.ru;

[¶]rovinskaya1950@mail.ru

The principal possibility of processing the industrial poor collective concentrates of platinum group metals (pgms) using a hydrocarbonyl technology with the selective concentration of pgms from poor multicomponent chloride and chloride-sulfate solutions with the subsequent production of pure pgms is shown.

1. Introduction

The pgms can be produced both from natural raw materials and treated pgm materials, including scrap metal and waste in the form of used platinum alloy products, electronic waste or coating materials. They may also be extracted from production induced sources, such as the byproducts of copper-nickel sulfide ore treatment. In all cases of pgm raw material treatment, production involves extracting pure pgms from multicomponent systems in which their content can vary considerably.

Extraction of pgms from natural and synthetic materials uses various technological processes, which include precipitation, extraction, sorption and electrochemical processes in various forms (1).

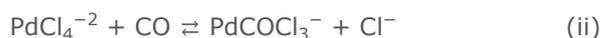
This study investigates fundamental technological possibilities of concentrating and separating pgms based on hydrocarbonyl processes that occur during

the treatment of solutions of pgm chlorocomplexes with carbon monoxide under atmospheric pressure (**Figure 1**).

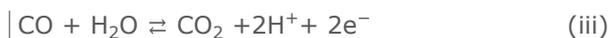
Carbon monoxide molecules have a high thermodynamic potential of a reducing agent. For example, for Reaction (i):



the ΔG° value amounts to -314.7 kJ. However, Reaction (i) does not occur spontaneously, due to high-energy chemical bonds between carbon and oxygen atoms. Nevertheless, in the presence of catalysts, carbon monoxide molecules are activated due to a change in the energy of bonding electrons, and the mixture of carbon monoxide with ambient oxygen gains chemical reactivity as per Reaction (i). For instance, when treating H_2PdCl_4 solution with carbon monoxide, the first stage is the insertion of a carbon monoxide molecule into the inner sphere of the PdCl_4^{-2} complex, thereby generating carbonyl chloride complex as per Reaction (ii):



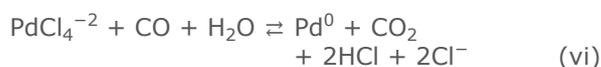
As the result of Reaction (ii), free molecules become ligands, which lead to their activation and provoke inner sphere redox process (Reactions (iii)–(iv)):



This is described by Reaction (v):



Reactions (ii) and (v) lead to palladium reduction by carbon monoxide, Reaction (vi):



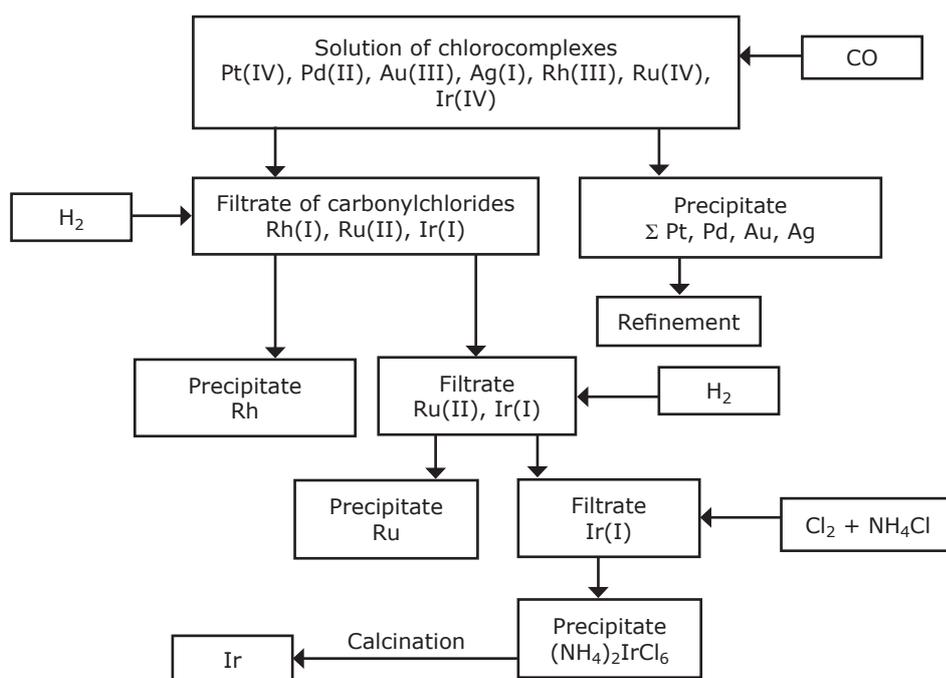
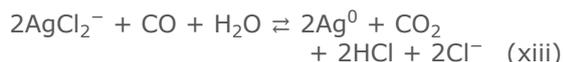
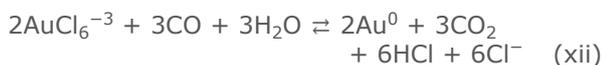
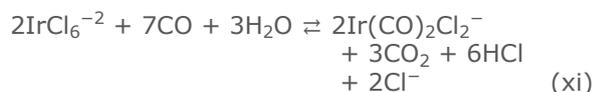
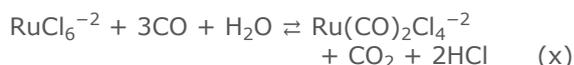
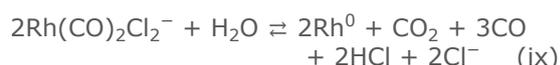
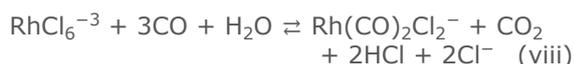
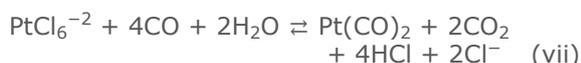


Fig. 1. Schematic of one of the options of the hydrocarbonyl processes of concentration and separation of precious metals

Reaction (vi) reflects the processes occurring in chloride pgm solutions during their treatment with a gas mixture containing carbon monoxide and depicts the nature of the 'hydrocarbonyl process' term (2).

The reduction of noble metals by treating their chlorocomplexes with carbon monoxide can be represented by Reactions (vi)–(xiii):



All these reactions are preceded by reactions in which chloride complexes are converted into various carbonyl chloride complexes. The latter can be further subjected to inner sphere redox processes generating either metals (Reactions (vi), (ix), (xii), (xiii)) or carbonyl chloride complexes in

which metals have low oxidation states (Reactions (vii), (viii), (x), (xi)).

The capacity of noble metals to enter a free state is defined by the following series: gold > palladium > platinum > rhodium (2).

This study explores the opportunities of applying hydrocarbonyl processes in the separation and concentration of pgms from multicomponent systems represented by the industrial lean bulk concentrates of pgms (copper and nickel anode sludges) and rich bulk concentrates of pgms (concentrates predominantly containing: (a) platinum and gold; (b) rhodium, ruthenium and silver; or (c) iridium).

The principles of hydrocarbonyl technology for the treatment of various pgm industrial concentrates as stated in (3), where copper-nickel anode sludges with the high contents of copper, nickel, iron, selenium and tellurium were used as primary products, have become a foundation for further feasibility studies of reprocessing lean and rich bulk pgm concentrates using hydrocarbonylation.

2. Experimental Section

Laboratory experiments on hydrocarbonyl processes were conducted using pgm chlorocomplex solutions generated from corresponding chloride reactants (standardised test solutions), chloride and chloride-sulfate solutions generated through the

hydrochlorination of industrial products, such as anode sludges generated during the extraction of cathode copper and nickel, and pgm concentrates used in refining.

Carbon monoxide was obtained by treating hot sulfuric acid with formic acid. After collecting, carbon monoxide was stored in gasometers. The reactions took place in glass reactors equipped with mechanical stirrers. Moreover, analytical support was provided through atomic absorption and chemical analyses.

2.1 Treatment of Lean Bulk pgm Concentrates

For this experiment, chloride and the chloride-sulfate solutions of industrial copper and nickel anode sludges were used. Their contents are listed in **Tables I** and **II**.

2.1.1 Treatment of Copper Anode Sludge Solution

Carbon monoxide was bubbled through 500 ml of a solution (see **Table I**) while stirring vigorously at 97–98°C and atmospheric pressure for 7 h. A black-coloured precipitate was obtained. The suspension was cooled down in carbon monoxide atmosphere and vacuum filtered. Thereafter, the obtained residue was washed with 2 M HCl. The obtained black precipitate was calcined at 900°C until a metal

sponge was formed (C-1). This was accompanied by the distinctive odour of SeO₂ and TeO₂. The obtained C-1 was dissolved in aqua regia and analysed for the content of noble and non-ferrous metals. Upon the analysis of the obtained solution, the content of C-1 was found to be as presented in **Table III**.

After the isolation of C-1, the filtrate was extracted with isoamyl alcohol at room temperature while stirring for 15 min in five stages with an aqueous-to-organic phase ratio of 5:1. Both extraction phases as well as wash waters from C-1 were analysed for the contents of noble metals. Their breakdown by conversion products is shown in **Table IV**. **Table IV** indicates that the consecutive processes of hydrocarbonylation and liquid extraction result in reasonably full extraction of noble metals from the copper anode sludge solution into two products: sufficiently selective C-1 and organic phase (isoamylic extract).

To define the parameters of the hydrocarbonylation process where the coprecipitation of rhodium with palladium and platinum in C-1 is eliminated, a series of experiments on the hydrocarbonylation of standardised test solutions containing chlorocomplexes platinum(IV), palladium(II), rhodium(III), ruthenium(IV) and iridium(IV) were conducted at various temperatures and hydrochloric acid concentrations. Obtained precipitates and filtrates were analysed for pgm content, which allowed the rate of pgm extraction

Table I Composition of Copper Anode Sludge Solution

Component	Content, g l ⁻¹	Component	Content, g l ⁻¹
Cu	~50.000	Pt	2.0000
Ni	~30.000	Au	0.2390
Fe	~3.000	Ag	0.3910
Cl⁻	214.000	Rh	0.2080
SO₄²⁻	67.500	Ru	0.0630
Pd	5.763	Ir	0.0104

Table II Composition of Nickel Anode Sludge Solution

Component	Content, g l ⁻¹	Component	Content, mg l ⁻¹
Cu	15.500	Rh	41.4
Ni	10.500	Ru	8.7
Fe	3.000	Ir	3.6
Cl⁻	179.500	Ag	86.7
SO₄²⁻	19.400	Au	0.2
Pd	1.304	Se	171.0
Pt	0.323	Te	102.0

to be defined for each product. Results are given in **Table V**. The analysis of these results shows that the coprecipitation of rhodium with platinum and palladium during the hydrocarbonylation of chlorocomplex solutions platinum(IV), palladium(II) and rhodium(III) does not occur at HCl concentrations $\geq 2 \text{ mol l}^{-1}$ and temperatures $\leq 80^\circ\text{C}$. These conditions were taken into account during the study of the treatment process of the nickel electrolyte sludge solution.

2.1.2 Treatment of Nickel Anode Sludge Solution

In a series of experiments, 0.5 l to 0.7 l of nickel anode sludge solution (see **Table II**) was treated with carbon monoxide under atmospheric pressure, temperature of 20–60°C and HCl concentration of 2.0 mol l^{-1} while stirring vigorously.

Obtained black-coloured finely dispersed precipitates were separated by filtration under

Table III Composition of C-1, Obtained by the Precipitation of Copper Anode Sludge Solution

Component	Content, wt%	Component	Content, wt%
Pd	64.41	Ru	not detected
Pt	24.58	Cu	0.042
Au	2.76	Ni	0.041
Ag	4.42	Fe	0.005
Rh ^a	2.48	SiO ₂	1.53
Ir	not detected	Σ	100.27

^aRh coprecipitates as a result of the high temperature of hydrocarbonylation

Table IV Breakdown of Noble Metals by Products Obtained from Copper Anode Sludge Solution Using Carbonyl Extraction Method

Metal	Content, % of the initial amount in copper anode sludge solution (see Table I)				
	C-1 ^a	Wash waters	Organic phase	Aqueous phase	Σ
Pd	99.97	0.42	0.03	0.04	100.46
Pt	98.32	1.69	0.03	not detected	100.04
Rh	103.90 ^b	not detected	1.15	not detected	105.02
Ru	not detected	7.63	73.00	not detected	80.63
Ir	not detected	not detected	115.20	not detected	115.20
Au	100.40	not detected	not detected	not detected	100.40
Ag	98.25	not detected	not detected	1.15	99.40

^aSe and Te are precipitated into C-1 almost completely and can be removed by calcination

^bRh precipitated into C-1 as a result of high hydrocarbonylation temperature

Table V Precipitation of pgm When Using Carbon Monoxide Under Atmospheric Pressure on Standardised Test Solutions Containing Chlorocomplexes Platinum(IV), Palladium(II), Rhodium(III), Ruthenium(IV), Iridium(IV)

No. of standardised test solution ^a	HCl, mol l ⁻¹	pgm concentration in standardised test solution, mg l ⁻¹					pgm precipitation rate, %				
		Pd	Pt	Rh	Ru	Ir	Pd	Pt	Rh	Ru	Ir
1	1.0	1364	290	76	46	54	100	100	21.0	traces	traces
2	1.4	182	430	192	92	108	100	100	1.2	traces	traces
3	2.0	62	326	48	46	54	100	100	0.1	traces	traces
4	2.0	62	326	48	46	54	100	100	0.03	traces	traces
5	2.5	62	326	48	46	54	100	99.9	traces	traces	traces

^a Hydrocarbonylation conditions:

No. 1. t = 100°C; for 2.5 h; bubbling, no stirring

No. 2. t = 100°C; for 3.0 h; bubbling, no stirring

No. 3. t = 80°C; for 3.0 h; bubbling, with stirring

No. 4. t = 50°C; for 3.0 h; bubbling, with stirring

No. 5. t = 50°C; for 3.0 h; bubbling, with stirring

vacuum and washed with 2 M HCl. These precipitates were analysed without calcination. **Table VI** lists the results of the analysis, which shows that reasonably a full separation of pgms into two selective products occurred: black fine precipitate containing platinum, palladium, gold, silver, selenium and tellurium; and solution containing rhodium, ruthenium, iridium and non-ferrous metals.

2.2 Treatment of Industrial pgm Rich Bulk Concentrates

Section 2.1 demonstrated the capability of extracting and concentrating pgms from the solutions of their lean bulk concentrates, for example copper and nickel anode sludges. At the same time, the capability of using hydrocarbonylation to treat the rich bulk concentrates of pgms is also of great technological interest. These concentrates

are represented by, in particular, three types (pgm concentrates predominantly containing: (a) platinum and palladium, M-1; (b) rhodium, ruthenium and silver, M-2; (c) iridium, M-3; and (d) speiss alloy). At present, the refinement of such concentrates is conducted under separate processes (1).

To conduct an experimental treatment through hydrocarbonylation, a total chloride solution obtained by the hydrochloration of concentrates M-1, M-2 and M-3 at the ratio of 4:2:1 was used. During the hydrochloration process of the concentrate mixture, silver was removed as AgCl precipitate. Thereafter, from the obtained solution, gold was extracted by treating it with $\text{Fe}_2(\text{SO}_4)_3$ solution. **Table VII** describes the content of the obtained solution. Within the experiment, carbon monoxide was bubbled through 20 ml of the original solution (see **Table VII**) under atmospheric pressure and temperature of 70°C while stirring vigorously for 3.33 h.

Table VI Composition of the Black Precipitate Obtained by the Hydrocarbonylation of Nickel Anode Sludge Solution (see Table II) ^a

Content, wt%	Item no.					Mean	pgm precipitation rate, %
	1	2	3	4	5		
Pt	14.63	16.12	14.72	14.70	17.19	15.47	98.0
Pd	67.00	66.17	67.35	66.20	66.75	66.69	99.9
Au	0.02	0.02	0.02	0.02	0.02	0.02	100
Ag	0.62	0.52	0.63	0.78	0.16	0.54	26
Rh	0.007	0.009	0.010	0.012	0.008	0.009	0.3–0.5
Σ Pt, Pd, Au, Ag, Rh	82.28	82.84	82.73	81.71	84.13	82.74	–
Se	9.61	9.90	10.10	9.73	8.95	9.86	95
Te	5.50	5.29	5.67	5.16	5.03	5.33	95
Σ Se, Te	15.11	15.19	15.77	14.89	13.98	14.93	95
Ni	0.020	0.004	0.019	0.012	0.009	0.013	–
Fe	0.009	0.020	0.037	0.018	0.024	0.022	–
Cu	0.12	0.16	0.26	0.23	0.19	0.19	0.02
Σ Ni, Fe, Cu	0.15	0.18	0.32	0.26	0.22	0.23	–
Σ^b total	97.54	98.21	98.82	96.86	98.33	97.95	–

^a Treatment conditions: PCO = atmospheric pressure; t = 20–60°C; treatment time 3–4 h

^b All precipitate contains approximately 1.50 wt% of SiO₂

The solution was observed to acquire black colour as a result of the generation of finely dispersed powders of palladium and platinum, which were easily filtered out with a vacuum filter. The filtrate was red and brown. The obtained precipitate was washed with 2 M HCl, dried and weighed. 0.5515 g of black-coloured powder was generated. The precipitate possessed large specific surface area and high absorbing capacity, thereby required thorough washing.

The analysis of the powder and filtrate for the content of palladium, platinum, gold, rhodium, ruthenium and iridium showed almost full precipitation of palladium, platinum and gold (none of the elements were found in the filtrate), no ruthenium and iridium were found in the powder, and the extraction rate of rhodium from the solution amounted to approximately 1%.

It is worth noting that platinum from the solution is not recovered as metal, but as its oligomeric dicarbonyl $[\text{Pt}(\text{CO})_2]_n$, where n is divisible by three. Palladium is extracted in its native form, together with its amorphous carbon phase (4).

In another experiment, 50 ml of the original solution (see Table VII) was treated with carbon monoxide under atmospheric pressure and temperature of 95°C for 4.5 h while stirring vigorously. Finely dispersed black powder was produced. After filtering, washing with 2 M HCl and air drying, 1.3501 g of a black powder were

recovered, which was analysed for the content of noble metals (Table VIII).

The filtrate, which was yellow and green, was extracted twice with 10 ml of isoamyl alcohol. The organic phase coloured in yellowish was boiled dry without calcination. The boiled organic phase was analysed for the content of noble metals (Table VIII).

The results of the laboratory treatment of the mixture of concentrates M-1, M-2 and M-3 show that the hydrocarbonylation process can be successfully used at the primary stage of refinement, and this allows to separate rhodium, ruthenium and iridium from other noble metals and makes the subsequent extraction of platinum and palladium, as well as rhodium, ruthenium and iridium easier.

To confirm the possibility of extracting rhodium, ruthenium and iridium using the traditional technology of the nitration of their carbonyl chloride solutions, which are left after extracting the concentrate of platinum, palladium, gold, tellurium and selenium by hydrocarbonylation, a process solution of speiss with the following content (g l^{-1}) was used: platinum, 20.02; palladium, 53.00; rhodium, 6.50; ruthenium, 0.50; iridium, 2.70; gold, 0.82; tellurium, 3.00; selenium, 2.30; copper, 16.40; lead, 3.70; bismuth, 3.85; nickel, 2.90; iron, 1.55; HCl, 100.00. Carbon monoxide was bubbled through 500 ml of the specified solution at 60°C under atmospheric pressure for 4 h while stirring vigorously. This generated the precipitate of Σ platinum, palladium, gold, selenium, tellurium, which was washed with 2 M HCl after the separation. The precipitate and filtrate were analysed for the content of original components. It was concluded that gold, palladium, selenium and tellurium precipitated fully whereas platinum precipitated by 98%. The solution after the precipitation of Σ platinum, palladium, gold, selenium, tellurium was nitrated with the precipitation of rhodium in

Table VII Composition of the Solution Obtained by the Hydrochlorination of M-1, M-2 and M-3 Concentrate Mixture after Silver and Gold Extraction

Content, mg l^{-1} ^a						
Pd	Pt	Rh	Ru	Ir	Au	HCl
18200	5440	615	160	200	1.65	85500

^a Se and Te contents were not defined

Table VIII Breakdown of pgm Byproducts Obtained with M-1, M-2 and M-3 Concentrate Mixture Chloride Solution

Product	Breakdown of metals byproducts regarding their content in the original solution (see Table VII), %					
	Pt	Pd	Au	Rh ^a	Ru ^b	Ir ^b
Black powder (precipitate after hydrocarbonylation)	~100	~100	~100	2.31	not detected	not detected
Organic phase of extraction	–	–	–	98.15	65.60	92.00

^a Rh coprecipitates due to the high temperature of hydrocarbonylation. Its presence can also be explained by the inadequate washing of the precipitate

^b Not the full transition of Ru and Ir to the organic phase of extraction is consistent with their breakdown ratio (2)

the form of its ammonium–sodium hexanitrate: $(\text{NH}_4)_2\text{NaRh}(\text{NO}_2)_6$.

Thus, the compatibility of hydrocarbonylation and the subsequent processes of the traditional saline extraction technology for rhodium, ruthenium, iridium (1) has been shown.

2.3 Sorptive Extraction of Rhodium, Ruthenium and Iridium

Technologies for the extraction of pgms from their chlorocomplexes utilise sorption on ion exchange resins (1). Thus, exploring the opportunity of using sorption for the solutions of carbon chloride anionic complexes $\text{Rh}(\text{I})\text{-Rh}(\text{CO})_2\text{Cl}_2^-$, $\text{Ru}(\text{II})\text{-Ru}(\text{CO})_2\text{Cl}_4^{-2}$ and $\text{Ir}(\text{I})\text{-Ir}(\text{CO})_2\text{Cl}_2^-$ to extract rhodium, ruthenium, iridium was appropriate.

To this extent, we used a solution of chlorocomplexes RhCl_6^{-3} , RuCl_6^{-2} and IrCl_6^{-2} containing (mg l^{-1}): rhodium, 260.3; ruthenium, 83.0; iridium, 63.8 and HCl , 2 mol l^{-1} , and a solution of carbonyl chloride anionic complexes rhodium(I), ruthenium(II) and iridium(I), obtained by treating a similar solution of chlorocomplexes RhCl_6^{-3} , RuCl_6^{-2} and IrCl_6^{-2} with carbon monoxide at 80°C for 2 h, which led the solution to change its colour from red and brown to yellowish, which is a distinct feature of carbonyl chloride anions rhodium(I), ruthenium(II) and iridium(I).

Both solutions were engaged with gel anion exchange resin based on the copolymer of styrene and divinylbenzene with benzene–pyridinium functional groups (ammonium molybdophosphate (AMP)) while stirring for 2 h. The solutions were then analysed for the content of rhodium, ruthenium and iridium. Results for the observed sorption rate are given in **Table IX**. The results given in **Table IX** show that the processes of

hydrocarbonylation and sorption are sufficiently technologically compatible.

2.4 Selective Extraction of Rhodium, Ruthenium and Iridium

Given the specific properties of carbonyl chloride complexes rhodium(I), ruthenium(II), iridium(I) (2), it was of interest to obtain the experimental results of their reaction with hydrogen under atmospheric pressure, as it is known that chlorocomplex solutions rhodium(III), ruthenium(IV), iridium(IV) only react with hydrogen at high pressure (5). For this experiment, a standardised test solution of chlorocomplexes rhodium(III), ruthenium(IV), iridium(IV) in 2 M HCl with the following metal concentration (mg l^{-1}): 168.0; 119.0; 70.0, respectively, was treated with carbon monoxide under atmospheric pressure and temperature of 95°C for 2 h. The solution was observed to quickly lose its original red and brown colour and turned a yellowish colour, which is a characteristic of carbonyl chloride complexes rhodium(I), ruthenium(II), iridium(I). Thereafter, at the same conditions, hydrogen was fed to the reactor instead of carbon monoxide. This provoked the solution to gain black colouration and precipitate. The hydrogen treatment lasted 6 h. The obtained precipitate was filtered out and dissolved in the mixture of HCl and H_2O_2 . The atomic absorption analysis of the precipitate and filtrate has shown that the resulting black precipitate comprised rhodium without ruthenium and iridium content, and that the filtrate contained almost no rhodium. The filtrate was neutralised to pH 5 and treated with hydrogen under the same conditions. The solution gained black colour and released a black precipitate. The hydrogen treatment lasted 6 h. The black precipitate was filtered out and dissolved in the mixture of HCl and H_2O_2 . The atomic absorption analysis of this solution showed that it contained ruthenium only, whereas the analysis of the solution after filtering out black ruthenium showed that there was almost no ruthenium in it. The yellowish filtrate was treated with chlorine gas, which produced intense red colouration characteristic for chlorocomplex iridium(IV). NH_4Cl in the form of saturated aqueous solution was added to this solution. This resulted in the black precipitation, characteristic for $(\text{NH}_4)_2\text{IrCl}_6$. The above-precipitate solution analysis showed trace amounts of iridium.

The described experiment has shaped a foundation for conducting a series of experiments aimed to

Table IX Results of Sorption of Chlorocomplexes Rhodium(III), Ruthenium(IV), Iridium(IV) and Carbonyl Chloride Complexes Rhodium(I), Ruthenium(II) and Iridium(I) by Anionic AMP Resin^a

Solution type	pgm sorption rate on anionic AMP resin, %		
	Rh	Ru	Ir
Chlorocomplexes	85.9	47.0	31.0
Carbonyl chloride complexes	80.3	66.3	55.3

^a Room temperature for 2 h and resin-solution ratio of 1:50

optimise pgm reduction processes, which allowed to formulate the method for selective extraction of rhodium, ruthenium and iridium from rhodium(I), ruthenium(II) and iridium(I) carbonyl chloride solutions by treating them with hydrogen under atmospheric pressure (6).

2.5 Impact of Carbon Monoxide Content in the Gas Mixture on pgm Reduction Rate

Reactions (vi)–(xiii) have some induction period ($T_{ind.}$), i.e. time from the beginning of the treatment of the pgm chloride solution with carbon monoxide until black pgm precipitation or change in original colour. The induction period of the hydrocarbonylation is impacted by temperature, stirring speed, partial pressure of carbon monoxide and H^+ and Cl^- ion concentration (2).

Studies were conducted to identify the impact of the carbon monoxide content in the reaction gas (P_{CO}) on the induction period of a hydrocarbonyl process. As an example, we provide the results of the studies on the impact of P_{CO} on the induction period of Reaction (vi) (Table X). The original H_2PdCl_4 solution contents were as follows: $[Pd(II)]$, 167 mg l^{-1} ; HCl, 2 mol l^{-1} ; solution volume, 75 ml; $CO + N_2$ mixture bubbling rate, 100 ml min^{-1} ; stirring speed, 1000 rpm; temperature, 50°C. The length of the induction period of Reaction (vi) was calculated based on the automatic logging of changes in the light transmission value of the solution.

The experimental data provided in Table X indicate that air-producer gas can be used for conducting hydrocarbonyl processes in technological operations, as the significant decrease in the hydrocarbonylation rate is observed when carbon monoxide content in the $CO + N_2$ mixture does not

exceed 20% whereas air-producer gas contains 25% of carbon monoxide.

3. Discussion of Results

The provided results of laboratory studies for the processes of the generation and breakdown of carbonyl pgm complexes, which take place when the solutions of their chlorocomplexes are treated with carbon monoxide under atmospheric pressure and cause pgm chlorocomplexes to turn into carbonyl chloride complexes with low oxidation state metals or to the full reduction of pgms, allow use of these processes to conduct selective pgm concentration from multicomponent solutions with the subsequent individual extraction of metals. This can become innovative in pgm hydrometallurgy.

A significant technological advantage of the hydrocarbonyl technology is the ability to separate original chloride and chloride-sulfate multicomponent solutions containing pgm in a wide concentration range (from tens of grams per litre to some milligrams per litre) and heavy non-ferrous metals in large amounts into two products. Platinum and palladium, along with gold, silver, selenium and tellurium, precipitate quite effectively, when rare pgms (rhodium, ruthenium and iridium) along with non-ferrous metals remain in the solution, transiting from their chlorocomplexes to carbonyl chloride anionic complexes where metals have low oxidation states: rhodium(I), ruthenium(II), iridium(I) with their specific properties, which makes the subsequent separation process easier.

Another advantage of the hydrocarbonylation process is that the separation of original multicomponent chloride solutions containing pgm into two products can be conducted in one step at the very beginning of the manufacturing process using only one reactant, i.e. cheap and available air-producer gas containing approximately 25% of carbon monoxide and 75% nitrogen in volume.

Moreover, several factors affect the results of the hydrocarbonyl processes; therefore, control possibilities for these processes can be extended to ensure that they occur as desired. This significantly distinguishes the hydrocarbonyl technology from all other technologies used in this field. Thus, it was demonstrated (2) for the Reaction (vi) that the palladium reduction rate has the following functional

Table X Impact of Carbon Monoxide and Nitrogen Gas Mixture Content on Reaction (vi) Induction Period

CO content in $CO + N_2$ mixture, vol%	100	70	50	33	16	8
Reaction (vi) induction period, $T_{ind.}$ S	58	62	65	67.5	70.5	135

dependence on the component concentration, Equation (xiv):

$$\frac{d[\text{Pd(0)}]}{dT} = f([\text{Pd(II)}], [\text{H}_2\text{O}]^2, [\text{H}^+]^{-2}, [\text{Cl}^-]^{-1}, P_{\text{CO}}^n) \quad (\text{xiv})$$

where $n = 0.5$ at $P_{\text{CO}} \geq 30$ kPa; $n = 1.0$ at $P_{\text{CO}} \leq 30$ kPa.

By changing the contents of the original solution along with the carbon monoxide content in the reaction gas and temperature, one can significantly influence the rate of hydrocarbonyl processes and their final result. Thus, when treating the palladium dichloride solution with carbon monoxide in 10 M HCl at 50°C, Reaction (vi) does not go to completion, and its colour changes from red and brown (original solution) to yellow and green. When caesium chloride crystals are introduced to the solution, small yellow and green crystals comprising $\text{Cs}[\text{PdCOCl}_3]$ are generated (2).

4. Conclusion

The results of this study demonstrate the technological potential of hydrocarbonyl processes for the selective concentration of pgms from multicomponent chloride–sulfate solutions with the subsequent production of pure metals. Furthermore, hydrocarbonyl processes can be combined with existing technologies, such as precipitation in the form of complex salts, extraction and sorption, which expands their technological application. This is supported by the results of our latest studies (6–9). Hydrocarbonyl processes are also of interest in the chemistry of pgms (4).

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The Authors



Professor Igor V. I. Fedoseev is Doctor of Technical Sciences and a graduate of the Chemical Faculty of the Lomonosov Moscow State University, Russia. He previously worked at Norilsk Nickel, Russia. He was engaged in the study of carbonyl chloride complexes of platinum metals and defended his thesis and doctoral dissertation in chemistry and technology of carbonyl chloride complexes of pgms. His area of scientific interest is the chemistry of carbonyl complexes of pgms and their technological use. He is the author of two monographs.



Yuriy A. I. Kotlyar, PhD (Technical Sciences), graduated from the Moscow Machine Tool Institute, Russia, with a degree in machines and foundry technology. He worked as General Director of RAO Norilsk Nickel, General Director of JSC Gipronickel Institute, Chairman of the Board of Directors of RAO Norilsk Nickel, Chairman of the Bureau of the Coordination Council of the Union of Scientific-Technical Society of Scientists, specialists in the production and processing of non-ferrous metals, gold and diamonds. He is a member of the Supervisory Board of the Golden Club of Russia, a lecturer at the Moscow Institute of Steel and Alloys, a State Prize Laureate and General Consultant of PJSC Norilsk Nickel.



Vasily V. Vasekin, PhD (Chemistry), General Director of Supermetal JSC, is a graduate of the Chemical Faculty of Lomonosov Moscow State University, Russia. He is engaged in metallurgy and chemistry of platinum alloys and materials based on them. He conducts research and develops technologies using composite materials based on platinum alloys in the production of glass-melting devices and catalytic systems.



Natalya V. Rovinskaya, PhD (Chemistry), Senior Researcher, is a graduate of the Lomonosov Moscow Institute of Fine Chemical Technology, Russia. She was engaged in the problems of synthesis of semi-synthetic antibiotics. She defended her thesis on the methods of synthesis of doxycycline. She is currently engaged in technological work on the separation of pgms from industrial wastes and their purification by hydrolytic methods and the development of methods for the analysis of pgms and their alloys.