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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Effect of Inorganic Compounds in the Activated Carbon Phase and in Solution on the Adsorption of Gold(I) Cyanide Complex

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Abstract—Inorganic impurities (ash) in the composition of activated carbons of the H-type (AG-90, WSC-208C, and Norit RO 3515) and their effect on the adsorption of $Na[Au(CN)_2]$ from alkaline cyanide solutions were studied. Variants of presorption acid washing of carbons to raise their reactivity in the sorption process of Au(I) recovery from cyanide solutions and pulps and the order of technological procedures for diminishing the loss of Au(I) and adsorbent were considered. The effect of some solution components on the adsorption kinetics of the noble metal was characterized.

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The widely accepted word combination "activated carbon" is a generalizing term that designates carbon substances differing in the nature of the starting raw materials, fabrication technology, chemical composition, and surface structure, as well as in the content of various impurities in the matrix. Activated carbon (AC) used in technological processes for sorption recovery of noble metals is most frequently produced from raw materials of vegetable origin: coconut shells, wood, brown and black coal, peat [1–3]. All these materials originally contain mineral impurities. For example, inorganic compounds in coconut shells are mostly represented by salts of alkali and alkaline-earth elements, iron, and aluminum. According to the data reported in the review [4], nut shells, the starting raw material for production of coconut activated carbon most widely used in the hydrometallurgy of gold, contain, in terms of the corresponding compounds, the following impurities (%) K_2O 0.226, Na_2O 0.127, CaO 0.017, MgO 0.016, $Fe_2O_3 + Al_2O_3$ 0.011, P_2O_5 0.030, S_3^{2-} 0.139, and Cl^- 0.324. After the carbonization and activation stages, the content of nonvolatile inorganic impurities in the coconut AC substantially increases.

The technology employed for manufacture of AC and, in particular, the so-called chemical activation of carbon materials frequently use various compounds serving as fire-retardants, modifying additives, and dehydrating agents: $ZnCl_2$, H_3PO_4, KOH, K_2S, Na_2CO_3, mixture of H_3BO_3 and $Na_2B_4O_7$, etc. [1, 3]. This also contaminates the product with inorganic substances. In addition to residual amounts of these compounds, secondary products can be formed in the AC matrix by interaction of these additives with atmospheric nitrogen, CO_2, and other substances. For example, KCN and K_2CO_3 have been identified as products formed in the carbon matrix by the chemical activation of a carbon of vegetable origin with KOH [5]. In manufacture of extruded granulated carbon sorbents, organic tars are used as binders [coke tar, wood-chemical tar, phenolformaldehyde tar, etc.]. These tars do not belong to the class of chemically pure products and commonly contain mineral impurities and, in particular, products of equipment corrosion. All these factors result in that industrially manufactured AC brands always contain inorganic compounds that form ash upon burning. The chemical composition of the ash appearing in the AC matrix already in carbonization and activation stages is determined by the type of raw material from which an AC is produced and by the technology of its manufacture.

In studies of the sorption properties of ACs with respect to noble metal compounds, a considerable attention is commonly given to functional groups on the carbon surface, porous structure of the sorbent, and charge of its surface. At the same time, the effect of inorganic impurities forming ash in the sorbent has been studied

Table 1. Composition of solutions obtained upon treatment of various types of ACs with water and 1 M acid solutions

AC brand	Treatment	Content in solution of indicated metal ions recovered from ACs, mg l^{-1}							
		Fe^{3+}	Cu^{2+}	Zn^{2+}	Mn^{2+}	Ca^{2+}	Mg^{2+}	K^+	Na^+
AG-90	HC1	1200	0.65	0.65	28.3	3200	900	47.0	42.9
Norit RO 3515	HC1	534	0.27	0.35	9.4	1100	280	1200	312
WSC-208C GR	HC1	26.2	0.023	0.10	1.48	82.7	103	2700	225
	H_20	<0.05	0.046	0.017	<0.05	1.2	0.43	4.9	98
	$HN0_3$	10.9	1.2	0.32	1.0	54.6	84.3	2400	205
	$HOS0_2NH_2$	9.9	1.3	0.37	0.97	56.7	87.6	2800	213

to a considerably lesser extent. Meanwhile, inorganic impurities (ash) in an AC affect its sorption activity [4], rather than playing the role of indifferent compounds.

In the course of the sorption process, the composition of mineral impurities in carbons changes. It has been shown that, in sorption recovery of Au(I) from cyanide solutions and pulps, the content of potassium and sodium in AC of G210 brand, produced from coconut shells, decreases by a factor of 4–5, and that of calcium becomes more than 7.5 times higher [6]. Thus, the composition of mineral components of the ash also depends on the ionic composition of a solution from which Au(I) sorption is performed. It is known that the AC capacity for $Na[Au(CN)_2]$ decreases as the CN- concentration in solution becomes higher, and presence of calcium and magnesium ions in solution leads to an increase in both the sorption rate and capacity of the carbon sorbent for the gold(I) cyanide complex [6–8]. It is believed that AC samples best suitable for sorption recovery of Au(I) from cyanide solutions and pulps contain 2–4 wt % ash [9].

The present study concerns the role of inorganic components in the AC matrix and in solution in adsorption of gold(I) dicyanoaurate complexes.

As objects of study served industrial AC samples of varied origin. The carbon of WSC-208C brand (Sutcliffe Speakman Carbons Ltd., UK) was produced from coconut shells. The starting raw material for manufacture of extruded AC of Norit RO 3515 brand (NORIT Activated Carbon, The Netherlands) is peat molded, after a special treatment and carbonization, with an organic binder [2]. The domestic extruded carbon of AG-90 brand (Zarya Open Joint-Stock Company, Russia) is produced from a mixture of black coal and half-coke, with a mixture of wood-chemical tar and coke tar as a binder [1].

To determine the cationic composition of the impurities, weighed portions of carbons from demonstration samples provided by manufacturing companies and unused in sorption processes were treated with a 1 M solution of acids (HCl, HNO_3, or $HOSO_2NH_2$). The acid solutions obtained on washing the ACs were studied by means of atomic-emission analysis with inductively coupled plasma (ICP). The results of the analyses are presented in Table 1.

As follows from the data in Table 1, the extruded carbons AG-90 and Norit RO 3515 markedly differ in the composition of metal cations recovered with the HCl solution from AC samples from the coconut carbon of WSC-208C brand. The main impurities in the matrix of the coconut carbon are compounds of alkali and alkaline-earth elements. At the same time, considerable amounts of iron(III) ions are recovered from extruded AC samples in addition to calcium, magnesium, potassium, and sodium ions.

Analysis of inorganic residues formed on burning various kinds of wood, to which coconut shells are genetically related, shows that cations of alkali and alkaline-earth elements also constitute the basis of ash-forming compounds [10]. The composition of the anionic part of ash compounds depends on the wood ashing temperature. For example, the main components of ash at 600°C are $CaCO_3$, $K_2Ca(CO_3)_2$, $Ca(OH)_2$, and MgO, whereas at 1300°C, ash mostly contains CaO and MgO and a minor amount of K_2SO_4 and Ca_2SiO_4 [10]. It should, however, be kept in mind that, in industrial manufacture of ACs suitable for recovery of gold(I) from solutions and pulps, the starting organic material is subjected to pyrolysis in the absence of oxygen at temperatures of 500–700°C and then is activated with superheated steam or carbon dioxide at 500–700°C [2]. Under these conditions, almost all organic compounds that originally contained inorganic compounds decompose. As a result, formation of the corresponding oxides, carbonates, and hydroxide in the AC matrix is the most probable. It has been shown that, in heating of an AC impregnated with

$CaCO_3$, full decomposition of calcium carbonate to give CaO occurs at 600–700°C [11]. The contact of potassium and calcium carbonates with superheated steam leads to their partial hydrolysis, which results in the formation of certain amounts of the corresponding hydroxides the carbon phase. In storage, the ash components present in the carbon phase and possessing basic properties absorb carbon dioxide from air, to be again converted into the corresponding carbonates. In addition, a possible source of CO_2 is the AC itself, whose surface is slowly oxidized (is aging) in air [12].

It should be noted that, even for samples with initially low ash content (0.10%), treatment of ACs with solutions of acids (HCl, HF, HNO_3, or successively HCl and HF) cannot fully remove ash, only its content in washed carbon diminished to 0.05–0.06% [13]. A similar situation is observed when AC samples taken after sorption of gold(I) from industrial cyanide solutions are washed with a mixture of 2.5% aqueous solutions of HCl and HNO_3. Washing with acids removes from AC nearly all sodium, potassium, and magnesium compounds and substantially diminishes the content of compounds of other metals, except iron [6]. In the last case, however, in contrast to a fresh carbon, iron compounds are present in the adsorbent phase as insoluble ferrocyanide salts, possibly polymers containing bridge cyanide ligands [14].

AC samples produced from saccharose and containing no ash are commonly divided into two groups: L- and H-carbons [4, 15]. Carbons of the first group are, as a rule, produced at carbonization and steam activation temperatures below 400°C. These carbons can adsorb strong acids from aqueous solutions. Occasionally, there are erroneous statements that the pH value of water-carbon suspensions is related to the presence of acid or basic functional groups on the AC surface. These statements are based on the fact that, in some cases, carbons produced at activation temperatures below 400°C can acidify water, with the pH value lowered to 2.5–4.0. At the same time, AC samples obtained at higher temperatures can alkalize water to values of 9.5–11.0 [16]. It should be emphasized that, whatever functional groups of acid or basic nature were present on the surface of AC samples, they cannot, in principle, noticeably change the pH value of the water–carbon suspension, unless, the water contains ions that can enter into ion exchange with groups on the adsorbent surface. It is noteworthy that H-carbons, whose representatives are examined in the present study, are commonly used to sorb cyanide complexes of gold(I) and silver(I) from solutions and pulps [9].

Under the conditions described in the experimental part of this communication, the activated carbons used in the study changed the pH of distilled water (pH_{in} 6.55) to the following values: AG-90 6.77, Norit RO 3515 9.17, and WSC-208C GR 9.50. Among all the three industrially manufactured AC brands, the weakest alkalization of the bulk aqueous phase is observed in its contact with AG-90 carbon. It is noteworthy that the content of K^+ and Na^+ ions in an extract obtained after treatment of this carbon with an aqueous HCl solution is also the lowest (Table 1). The results obtained suggest that the pH of water increases when the commercial carbons under study are placed in it, because soluble compounds Na_2CO_3, NaOH, K_2CO_3, KON, and, possibly, trace amounts of $Ca(OH)_2$ are washed-out from these carbons, in agreement with the data in Table 1. The appearance of potassium and sodium hydroxides in the aqueous solution may also be due to an exchange interaction of alkali metal carbonates with calcium hydroxide, the product formed together with calcium oxide in vapor-phase activation of carbons and further hydration of CaO in storage in air or in contact with water.

Naturally, the observed acidification of the aqueous suspension of ACs is due to the presence in their composition of soluble low-molecular-weight products of full or partial oxidation of the carbon matrix. Carbon dioxide and oxalic acid have been identified among these products [15].

Among the parameters of carbons, recommended in the literature for choosing an AC for sorption recovery of gold(I) from cyanide solutions and pulps is the equilibrium capacity of the carbon for gold(I) under the standard conditions, *k* (mg Au/mg carbon) [11, 16]. A multifactor correlation analysis demonstrated that the only parameter of carbons that correlates with k is the pH value of the aqueous suspension of AC, prepared with distilled water (correlation coefficient 0.598) [16]. In this case, the larger *k*, the higher the pH value of the aqueous suspension of this carbon. Although no correlation between the total content of ash in an AC and the pH of its suspension has been found {the correlation coefficient is as small as 0.072) [16]}, a statistically significant correlation between the water-soluble part of ash and the pH of the suspension must exist.

Insoluble organic compounds in the carbon phase, as well as cations and anions present in a solution, must strongly affect the sorption activity of an AC with respect to the cyanide complex. Such compounds as $CaCO_3$, $[Mg(OH)]_2CO_3$, and $SiO_2 \cdot nH_2O$ can mechanically block active sorption centers of ACs and thereby diminish their activity. An additional, and in many cases the main, source of calcium carbonate precipitated in the AC phase are calcium ions that appear in cyanide solutions and pulps as a result of dissolution of the alkaline reagent, $Ca(OH)_2$, used to preclude hydrolysis of NaCN. Insoluble calcium compounds in the AC phase do not adversely affect the sorption of the gold(I) cyanide complex at concentrations of up to 20 kg t^{-1}, whereas higher concentrations of calcium-containing substances (40–60 kg t^{-1}) hinder the sorption recovery of the noble metal [17].

It should be noted in this context that activated carbon thoroughly washed with acids to remove inorganic impurities has nearly zero sorption capacity for high-charge complex cyanide anions with Cu(I), Zn(II), Cd(II), etc. [18], in contrast to cyanide complexes of Au(I) and Ag(I). At the same time, analysis of saturated carbons taken from a real hydrometallurgical process shows that these carbons contain considerable amounts of cyanide compounds of Cu(I), Ni(II), Co(III), and Fe(III) [7]. It is not improbable that these compounds are formed via a heterophase exchange reaction with, e.g., $CaCO_3$ present in the carbon phase in the case when the corresponding calcium metallocyanate is less soluble than the initial carbonate. It is also noteworthy that, as observed in [19], the sorption capacity for Pb(II) ions of a charcoal washed with an HCl solution to remove ash is considerably lower than that of unwashed charcoal. The authors of [19] attribute this fact to adsorption of Pb(II) on magnesium and manganese oxides present in the carbon phase. The same positive influence can be exerted by ash components contained in ACs on the sorption of phenols from aqueous solutions [20]. Thus, ash in an AC can exert not only a depressive, but also an activating influence on the adsorption process.

Table 2. Effect of methods for pretreatment of WSC-208C GR activated carbon on the kinetics of $Na[Au(CN)_2]$ sorption from a model solution

AC pretreatment	k', h^{-1}	n
Fresh AC, no treatment	894	0.849
Treatment:		
water for 24 h	746	0.674
1 M HC1	1298	0.608
1 M HNO_3	406	0.502
1 M $HN0_3$*	697	0.216
1 M HNO_3**	914	0.633
1 M $HOS0_2NH_2$	1081	0.620
1 M $HOSO_2NH_2$*	1233	0.665
1 M $HOS0_2NH_2$*	1659	0.837

* Addition of solid $NaClO_4$ to the solution for creating a fixed ionic strength, increased as compared with the starting solution.

** Addition of solid $Ca(NO_3)_2$, instead of $NaClO_4$, to the solution in an amount corresponding to the ionic strength of the solution with sodium perchlorate

Presence of calcium and magnesium ions in cyanide solutions containing $[Au(CN)_2]^-$ ions improves the kinetic characteristics of Au(I) sorption on ACs [6–8]. It is the adsorption kinetics that is one of the two fundamental factors governing the choice of a particular AC brand for Au(I) recovery from cyanide solutions and pulps [21]. That is why the effect of the acid and aqueous washing of ACs and also that of calcium ions present in solution, on the sorption activity of the carbons under study was examined in more detail. The related experiments were carried out in a thermostated installation similar to that described previously [22]. As characteristics of the sorption activity of carbons served the pseudokinetic sorption constant k' (h^{-1}) and experimental parameter n, found from the equation $\log (\Delta[Au]_c^t/\Delta[Au]_s^t) = n \log t + \log k'$, where $\Delta[Au]_c^t$ is the change in the Au(I) concentration in the carbon phase with respect to the instant of time $t = 0$ (g ton^{-1}); $\Delta[Au]_c^t$ Au(I) concentration in solution at instant of time t (mg l^{-1}); and t, time (h) [23].

First, it was found that, if the gold-containing solution is fed into the chamber with carbon at a rate exceeding 720 ml min^{-1}, k' becomes independent of the circulation rate, which indirectly indicates that the sorption process occurs in this hydrodynamic mode under inner-diffusion control. For this reason, all the subsequent experiments were carried out with the $Na[Au(CN)_2]$ solution circulated at a rate of 1060 ml min^{-1}.

The results obtained in determining the parameters k' and n for WSC-208C GR ACs pretreated by various methods are listed in Table 2. It is assumed that AC samples best suitable for sorption of gold should have k' values exceeding 800 and $0.6 < n < 1.2$ [21, 22].

As can be seen in Table 2, a preliminary contact of a fresh AC with distilled water for 24 h markedly impairs the sorption kinetics of the Au(I) cyanide complex. Probably, this occurs for at least two reasons.

First, the adsorbent undergoes accelerated aging in water containing dissolved oxygen, which is manifested in that the adsorption centers of the AC are oxidized and the content of bound oxygen on its surface increases [24]. It has been convincingly demonstrated that the overall increase in the oxygen content of AC samples leads to a decrease in their adsorption capacity for gold(I) cyanide complexes [25].

Second, as already noted, it is not improbable that a part of micropores of the sorbent becomes inaccessible to$[Au(CN)_2]^-$ anions because of the reprecipitation of calcium carbonate on the AC surface via an exchange reaction of sodium and potassium carbonates passing from ash into solution with calcium hydroxide. A similar depression of the Au(I) adsorption can be caused by hydration of the surface of some poorly soluble components of ash within micropores of the sorbent or its complexation with ligands from solution, e.g., formation of FeO(OH) on the surface of Fe_2O_3 [19]. Processes of this kind may be accompanied by coarsening of ash particles and clogging of micropores of the sorbent.

The data in Table 2 demonstrate that the acid washing of a carbon before sorption of gold(I) cyanide complexes can change the kinetics of their subsequent sorption. In practice, the acid washing of a carbon is carried out either before desorption of Au(I) from the carbon, or (more rarely) after the desorption, before its thermal regeneration [8, 9, 11]. The available published data [26] demonstrate that, at least in some cases, acid treatment of an AC before the desorption of Au(I) from a saturated carbon makes it possible to recover a 3% larger amount of the metal, compared with the case when no operation of this kind is performed before desorption.

When choosing the place of the acid washing in the technological scheme, it is necessary, in addition, to take into account that calcium compounds [17] and Au clusters [27] catalyze the synthesis of water gas, whose formation leads to loss of the carbon sorbent. Gold clusters can be formed in the AC phase in its thermal regeneration at temperatures higher than 240°C [28] from cyanide complex particles remaining within micropores of the sorbent because of their being "sealed" by ash in the case when no preliminary acid washing of the carbon is carried out. For this reason, it is more pragmatic to perform an acid treatment of ACs before desorption of the cyanide complex of gold.

In acid washing of ACs under industrial conditions, 3.0–10.0% (more frequently, 3.0–3.5%) HCl solutions or 3.0–3.5% HNO_3 solutions are commonly used [11]. At equal concentrations (1.0 M) of the acid solutions, preliminary washing of ACs with a hydrochloric acid solution leads to an increase in the pseudokinetic sorption rate constant k' for a fresh carbon in the subsequent sorption of the gold(I) cyanide complex. The value of k' increases as compared both with the initial untreated carbon and with a sample preliminarily washed with distilled water (Table 2). By contrast, preliminary washing of a fresh AC with nitric acid diminishes the pseudokinetic sorption rate constant of the $[Au(CN)_2]^-$ anion. In this regard, use of HCl instead of HNO_3 in the stage of acid washing of the carbon is preferable. However, hydrochloric acid is more volatile and corrosive to equipment than nitric acid, which makes its use less convenient. At the same time, to preserve high kinetic characteristics of ACs toward $Na[Au(CN)_2]$ after washing with nitric acid, it is necessary to deliver carbon to thermal regeneration (reactivation) after each desorption procedure, which involves additional loss of the adsorbent [21].

The problem associated with the choice of an acid for AC washing is of particular practical interest and, therefore, it will be considered in more detail. As follows from the data in Table 1, all the acids used to treat samples of WSC-208C GR carbon have nearly the same efficiency as regards removal of ash components. However, there is a difference between nitric acid, on the one hand, and hydrochloric and sulfamic acids, on the other, in the redox properties toward both the AC matrix and the gold(I) cyanide complex adsorbed on the AC.

Aqueous solutions of HCl and $HOSO_2NH_2$ can protonate carbon atoms of the basal planes of AC via donor-acceptor interactions [29]. However, it would be expected that the presence of dissolved atmospheric oxygen in the aqueous solution of HCl should result in a more intense oxidation of the AC surface by this oxygen, compared with the case of a direct contact with air, because of the formation of hydroxy radicals in the $AC–O_2–H_2O$ system [24, 30]. Indeed, the content of bound oxygen on the surface of an AC substantially increases upon its contact with an HCl solution [13]. In addition, it has been shown that, after treatment of AC with a 1 M HCl solution at 60°C, chlorine atoms covalently bound to the carbon matrix appear on the AC surface [13]. This indicates that molecular or atomic chlorine is formed in the system as an intermediate product. Its appearance can be attributed to oxidation of the chloride ion under the action of $OH^{\cdot}$ radicals formed in solution in the presence of ACs [30]. This suggestion is also supported by the fact that, in treatment of ACs with an aqueous solution of HF under similar conditions, fluorine atoms are not incorporated into the carbon matrix [13] because fluoride ions cannot be oxidized under the action of hydroxy radicals. At the same time, the AC surface is enriched with oxygen upon treatment with an aqueous solution of HF, as also in the case of an aqueous solution of HCl [13, which does not contradict the above suggestions.

Heating of an aqueous solution of $K[Au(CN)_2]$ with 2 M HCl to boiling leads to precipitation of $[AuCN]_\infty$ [31]. Also, there is experimental evidence that $[Au(CN)_2]^-$ species adsorbed on carbon are converted to polymeric gold(I) cyanide $[Au(CN)]_\infty$ or oligomer$Au_4(CN)_5^-$-$[Au_x(CN)_{x+1}^-]$ upon treatment of a saturated AC with an HCl solution or upon sorption by AC of the $[Au(CN)_2]^-$ anion from acid solutions [25, 32–34]. However, it has been shown [35] that, at least in some cases, this conversion can indeed be associated with decomposition of a sample during its preparation for a physicochemical study. In addition, it has been demonstrated [35] that treatment of an AC with adsorbed complex anions $[Au(CN)_2]^-$ with an HCl solution at 60°C in air is accompanied by oxidation of a part of adsorbate ions to give adsorbed compounds of Au(III) that contain the $[Au(CN)_2Cl_2]^-$ anion. The adsorbed $[Au(CN)_2]^-$ anion can be oxidized under direct action of the hydroxy radical formed in the system AC–O_2–H_2O [with the subsequent replacement of water molecules in the inner sphere of the complex with gold(III) by chloride ions in the acid medium], or via the stage of oxidation of chloride ions by $OH^{\cdot}$ radicals [30] to give Cl_2 molecules, with their subsequent oxidative addition [31].

It can be recommended, on the basis of the presented material, to wash ACs saturated with gold(I) with cold solutions of acids, avoiding the heating of the system. Otherwise, it may become necessary to perform desorption with a solution that contains NaCN in addition to NaOH. These recommendations coincide with those reported previously [36].

It should be remembered that the use of hydrochloric acid in the stage of AC washing can create, in addition to difficulties associated with the corrosion activity and volatility of the acid, those with cyanidation of gold in autoclave oxidation of ores and concentrates because of the accumulation of chloride anions in return solutions [37]. This is particularly dangerous in processing of materials that contain natural carbonaceous substances. The carbonaceous materials themselves are subjected in autoclave conditions to partial hydrothermal activation, being converted to a certain extent to analogs of finely dispersed activated carbon. The $[AuCl_4]^-$ anion formed in autoclave treatment under severe conditions (temperature 190–225°C, partial oxygen pressure 0.3–0.7 MPa, $pH < 2$) in the presence of Cl^- and $FeCl_4^-$ ions are spontaneously reduced from solution on the surface of carbonaceous particles to metallic gold. Further cyanidation almost does not lead to the dissolution of the thus deposited metal, which may result in a substantial loss of gold [38, 39].

As regards removal of mineral ash components from the carbon phase, dilute HCl and HNO_3 solutions behave equally effectively [11], which is also confirmed by the data in Table 1. Similarly to HCl molecules, HNO_3 molecules are involved in donor-acceptor interactions with carbon atoms [40]. However, treatment of an AC with an HNO_3 solution leads to a considerably stronger, compared with HCl, increase in the concentration of bound oxygen throughout the carbon matrix, mostly in the form of functional groups with pronounced acid properties [41, 42]. It has been shown that the use of a 3% aqueous solution of HNO_3 at room temperature does not noticeably disturb the porous structure of an AC. If, however, the AC is treated with ~6% HNO_3 under heating to 60°C, the AC surface is oxidized, which is accompanied not only by an increase in the number of oxygen-containing groups of acid nature, but also by a decrease in the specific surface area and in the number of micropores in the sorbent [13]. This adversely affects both the sorption kinetics of Au(I) cyanide complexes and the capacity characteristics of the carbon [43].

Depending on the treatment conditions, the interaction of HNO_3 with the AC may lead to the formation of intercalation nitrate compounds of the type $C_{24}^+(NO_3)^- \cdot 3HNO_3$ [44], to direct oxidation of the carbon to give oxygen-containing functional groups on its surface [41, 42, 45, 46], or to an electrophilic attack of the nitronium cation on C–H moieties of the condensed aromatic system of the adsorbent, with the nitro group $-NO_2$ fixed on the carbon matrix [42, 45, 47]. It may also be assumed that inclusion compounds are formed in the AC phase with inorganic nitrates and hydroxo nitrates of inorganic components of ash, blocked in carbon micropores. The previously reported observation of the nitrate anion in the product formed in treatment of ACs with a concentrated solution of nitric acid may be due to this phenomenon or to intercalation of HNO_3 molecules into the carbon matrix.

It is of interest to note the results of the study [46] concerned with the influence exerted by a nitrating mixture composed of nearly 100% HNO_3 and H_2SO_4 on activated carbon fibers (ACFs). It was found using X-ray photoelectron spectroscopy (XPS) that signals with binding energies E_b N 1s of 400.0 and 401.8 eV appear in the spectrum of a sample treated with the mixture [46]. Commonly, signals with such binding energies are attributed to nitrogen atoms in pyrrole-like [24, 48] and quaternary [29] or pyridine-like groups [24, 49]. It is not improbable that the reason why these signals appear in the material studied in [46] is not related to the effect of nitric acid on ACFs, but can be attributed to the presence of dissolved atmospheric nitrogen in the system [24, 30, 50].

Sulfamic acid $HOSO_2NH_2$ is largely devoid of disadvantages associated with the high corrosion activity and volatility of HCl. In contrast to HCl, sulfamic acid cannot form, when oxidized by OH· radicals, compounds of the type of pseudohalogens, which add at sorption-active centers of AC. As can be seen in Table 1, sulfamic acid is almost not inferior to hydrochloric, or nitric acid in the amount of inorganic impurities extracted from ACs. Inorganic calcium and magnesium salts of this strong acid, unoxidizing the AC surface, are well soluble, and it can form fairly stable complex compounds with ions of transition elements. As follows from the data in Table 2, values of k' and n for $HOSO_2NH_2$ are only slightly inferior to the corresponding values for HCl, but markedly surpass those obtained with HNO_3. Therefore, sulfamic acid can be recommended as an alternative to hydrochloric acid.

Thus, it is advisable to subject a fresh AC introduced into the sorption process of Au(I) recovery from cyanide solutions and pulps not only to a preliminary mechanical conditioning [21], but also to an acid treatment to remove ash components. Therewith alongside dilute HCl solutions $HOSO_2NH_2$ solutions can be used for this purpose and even be preferable. It is advisable to use these same acids also in acid treatment of gold-saturated ACs before their delivery to the stage of desorption of the noble metal.

As a rule, gold is leached from ores and concentrates with aqueous solutions of NaCN at pH 10.2–10.7. In this case, inexpensive lime serves as the main agent that precludes hydrolysis of the NaCN solution. Because of the comparatively low solubility of calcium hydroxide introduced into the system and products formed in leaching, the concentration of calcium ions in return solutions does not exceed 800 mg l^{-1}. Occasionally, the more expensive sodium hydroxide is used instead of calcium oxide. However, in the opinion of certain researchers [17], NaOH may be preferable to $Ca(OH)_2$ for sorption of gold(I) cyanide complexes on ACs and electrolytic recovery of gold from solution.

In a closed technological water circulation scheme, salts accumulate in solutions, which leads to an increase in the ionic strength of these solutions. The sorption rate and the capacity of ACs for the cyanide complex of gold(I) depend not only on the ionic strength of a solution, but also on the nature of cations and anions it contains [6–8]. Therefore, the effects of sodium and calcium salts on the adsorption of the cyanide complex of gold(I) by AC samples preliminarily washed with HNO_3 and $HOSO_2NH_2$ solutions to remove ash were compared under conditions of a kinetic experiment (Table 2) at the same ionic strengths of a solution. $NaClO_4$ served as a sodium salt that raises the ionic strength of a solution, including the case when $Ca(NO_3)_2$ was introduced into it. Sodium perchlorate was added in the solid form to a $Na[Au(CN)_2]^-$ containing cyanide solution, with a 0.019 M concentration of $NaClO_4$ created. As can be seen from the data in Table 2, an increase in the ionic strength of the solution leads to a rise in k' and n for AC samples treated with both nitric and sulfamic acids. In the latter case, however, values of k' and n are substantially larger, which points to a higher reactivity of the AC treated with $HOSO_2NH_2$ toward the gold(I) cyanide complex.

An even stronger positive influence on the values of k' and n for both AC samples is exerted by addition to a solution of calcium ions in the form of $Ca(NO_3)_2$ (0.006 M) at the same ionic strength as that in the case of sodium perchlorate additive. It should be noted that presence of Ca^{2+} ions in solution not only positively affects the sorption kinetics, but also raises the AC capacity for the $[Au(CN)_2]^-$ anion [7]. This effect of Ca^{2+} ions on the sorption of gold(I) cyanide complexes by activated carbon is commonly attributed to deposition of neutral or positively charged associates $\{Ca[Au(CN)_2]_2\}$, $\{Ca[Au(CN)_2]\}^+$ or the corresponding solvent-separated ionic triads or pairs at sorption centers of the AC surface negatively charged in alkaline solutions [2, 6, 9, 17, 51–53].

It has been reliably established, using IR, NMR, and XPS spectroscopy, that gold(I) adsorbed on ACs from alkaline cyanide solutions is in the form of the dicyanoaurate anion [32, 35, 54]. However, there is experimental evidence that contradicts the concept according to which the $[Au(CN)_2]^-$ anion being adsorbed passes from solution into the carbon phase in the form of ionic associates and is present in the AC as a ionic triad with a calcium cation [35, 55].

In parallel, the amounts of Au(I) and Ca(II) absorbed by WSC-208C GR carbon samples pretreated with nitric (AC-N) and sulfamic (AC-S) acids were determined under kinetic-experiment conditions (Table 2). During 180 min of experiment, 1 g of AC-N carbon adsorbed 3.0 mg of gold(I) and 12 mg of calcium (molar ratio of the absorbed elements, Ca/Au = 19.7), and AC-S, 7.5 and 20.0 mg, respectively (Ca/Au = 13.2). It follows from these data that a larger amount of absorbed calcium corresponds to a larger amount of absorbed Au(I); however, the molar ratio of these elements in the AC phase markedly changes on passing from AC-N to AC-S. It should be noted that the results obtained strongly differ from the data reported by Tsuchida et al. [56], who demonstrated that the Ca/Au molar ratio on the carbon does not exceed unity. At the same time, the data obtained in the present study are in agreement with the results of Davidson's experiments [6].

Calcium ions can be bound to acid groups of the AC matrix, thereby changing the surface charge of the adsorbent in the alkaline medium from negative to positive. Ca^{2+} ions differ in this regard from single-charged sodium cations, which cannot recharge the AC surface under the same conditions [52]. The number of groups with pronounced acid properties must be substantially larger for AC-N, compared with AC-S [41, 42]. At the same time, quantum-mechanical calculations show that a calcium ion adsorbed by AC from solution may be situated on the sorbent surface separately from the $[Au(CN)_2]^-$ anion, but governs the adsorption of this anion.

Thus, calcium ions present in solution favor sorption of $[Au(CN)_2]^-$ ions by activated carbon and even compensates to a certain extent for the decrease in the kinetic sorption parameters k' and n on using nitric acid for acid washing of AC. However, use of hydrochloric or sulfamic acid in the stage of acid washing of a carbon before desorption of gold and subsequent thermal regeneration of the carbon, as well as replacing NaOH as an alkalizing agent with CaO, yields the maximum effect when performing CIP and CIL processes.

EXPERIMENTAL

The solutions obtained upon treatment of AC samples with acids were analyzed on a Baird 2000 atomic-emission spectrometer with inductively coupled plasma. The concentration of gold(I) in cyanide solutions was found using a SpektrAA 220 Varian atomic-absorption spectrometer.

The pH of aqueous extracts obtained on treating weighed portions of ACs with distilled water were measured with an accuracy of ±0.05 pH units with an I-500 ion meter. The aqueous extracts from ACs were prepared by the known procedure [16]. For this purpose, a 2.00-g portion of an AC was treated in a closed Erlenmeyer flask with freshly distilled water (200.0 ml) for 10 min under agitation on a PE-6410 laboratory vibration table. The solution separated from carbon by filtration was analyzed for the content of dissolved metal ions by the ICP method. AC samples were washed to remove the acid in the course of 10 days with 200-ml portions of distilled water under agitation on a vibration table. Distilled water was replaced with a fresh portion once a day. A control sample of WSC-208C GR AC was treated under the same conditions first for 24 h, and then for 10 days, with only distilled water. Washed carbon samples were dried in a desiccator to constant weight at room temperature.

The adsorption kinetics of the gold(I) cyanide complex was studied at a temperature of 26.0 ± 0.1°C. The sorption column was charged with a 0.500-g portion of a carbon and 500 ml of a standard solution containing 9.9 ± 0.2 mg l^{-1} of gold(I) in the form of $Na[Au(CN)_2]$, and 0.337 g l^{-1} of NaCN (pH 10.1) was poured into a flask. After that the whole system was thermostated for 40 min and then the cyanide solution was pumped through the column. To study the influence exerted by an increase in the ionic strength and by presence of calcium cations on the rate of gold(I) adsorption by the activated carbon, weighed portions of dry salts $NaClO_4$ and $Ca(NO_3)_2$ were introduced into the starting solution. Both the salts were of pure grade. During all the experiments, the temperature was maintained constant with a Thermo Haake DC30 thermostat. The solution was fed into the sorption column at a rate of 1060 ml min^{-1} by a Masterflex 7536-34 peristaltic pump. Samples of the solution circulated through the sorption column (5.0 ml) were taken for determining the residual concentration of gold(I) in 15, 30, 60, 120, and 180 min.

The $Na[Au(CN)_2]$ solution used in kinetic experiments was produced by treating a weighed portion of fulminating gold [58] with an excess amount of a NaCN solution under heating.

CONCLUSIONS

(1) Activated carbons of WSC-208C GR brand, fabricated from coconut shells, contain in their ash a lesser amount of transition metal compounds, but a greater amount of potassium compounds than extruded AG-90 and Norit RO 3515 carbons. The composition of the inorganic impurities widely varies between carbons of different nature. The main forms in which metals are present in ash are the corresponding carbonates, oxides, and hydroxides.

(2) Removal of ash components from the matrix of activated carbons increases their reactivity in the adsorption process.

(3) It is preferable to use acids having no oxidizing properties with respect to the carbon matrix for removing ash from activated carbons. The most convenient reagent for this process is sulfamic acid. The acid washing of activated carbons should be performed at normal temperature without heating of the acid solution. The acid treatment of a carbon saturated with gold(I) cyanide complexes should precede desorption of Au(I) and thermal regeneration of a desorbed carbon.

(4) In addition to mechanical conditioning before the first introduction into the sorption process, fresh activated carbons should be subjected to acid washing, which improves the kinetics of Au(I) sorption from cyanide solutions and pulps.

(5) The adsorption of the $[Au(CN)_2]^-$ anion by an activated carbon from a cyanide solution is accompanied by co-adsorption of considerable amounts of the Ca^{2+} cation. As regards the sorption kinetics of gold(I) cyanide complexes, use of $Ca(OH)_2$ as an alkaline reagent in the technological process of cyanide recovery of gold from ores and concentrates is preferable to that of NaOH.

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