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Readily Recoverable Sorbent For Gold Extraction.

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ABSTRACT

Synthesis of readily recoverable polyfunctional anion exchange resin has been developed with the aim of gold extraction by ammonolysis of styrene and acrylonitrile terpolymer by diethylene triamine with subsequent partial alkylation by sodium salt of monochloroacetic acid. Capacity and selectivity of the sorbent is adjusted by dilution of polymer matrix with "inert" styrene. Comparative tests demonstrate similarity of major properties of the obtained anion exchange resin and commercial foreign analog: PuroGold S 992.
Keywords: synthesis, polyfunctional anion exchange resin, acrylonitrile, styrene, cyanide, desorption of gold.

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INTRODUCTION

Experience of operation of gold mining companies of Russia and CIS countries, where gold is sorbed from cyanide-containing mediums by AM-2B anion exchange resin or its analogs, revealed that together with their high sorption properties these sorbents have certain significant drawbacks related mainly with difficulties of recovery [1]. Upon recovery of AM-2B, which includes eight procedures with total duration up to 240 hours, the medium composition varies from alkaline-cyanide to acid-thiourea with subsequent treatment by alkali; toxic hydrogen cyanide is evolved at this stage. Such mode leads to accelerated degradation of sorbent and corrosion of equipment.

In 2001-2008 PUROLITE company (Great Britain) developed weakly basic anion exchange resin, known as Purogold S 992 [2]. According to our data this sorbent is made on styrene matrix and contains mainly secondary amine groups. Its gold holding capacity is by 30-35% less than that of Russian AM-2B, however, desorption of gold by 95-96% is carried out in one contact by hot alkaline-cyanide solution, which, after extraction of gold, can be reused for ore leaching. Commercial approbation of Purogold S 992 at Pioner gold recovery plant, OAO Pokrovsky Mine, proved the efficiency of application of weakly basic anion exchange resin for gold extraction: capital costs decrease by 35%, operational costs -- by 85-90%. operation cycle of the sorbent decreases by three times, and throughput of equipment increases [1]. It is also established that selectivity of weakly basic anion exchange resin to gold is significantly higher than that of strongly basic ones.

The process can be described by the following equations:

$$\mathrm{Res-N(CH_3)_2 + HCl \rightarrow Res-N(CH_3)_2 \cdot HCl}$$
$$\mathrm{Res-N(CH_3)_2 \cdot HCl + Au(CN)_2^- \rightarrow Res-N(CH_3)_2 \cdot HAu(CN)_2 + Cl^-}$$

where Res is the polymer fragment.

Desorption of gold from saturated weakly basic anion exchange resin runs easily upon treatment by alkaline solutions (acid--base hydrolysis):

$$\mathrm{Res-N(CH_3)_2 \cdot HAu(CN)_2 + OH^- \rightarrow Res-N(CH_3)_2 + Au(CN)_2^- + H_2O.}$$

In order to organize import-substituting production of sorbent, such as Purogold S 992, characterized by similar properties, the experts of JSC “VNIIHT” developed procedure of synthesis of weakly basic polyfunctional anion exchange resin conventionally referred to as Rossion-15.

Weakly basic anion exchange resins are comprised of primary, secondary, and tertiary amine groups and exchange anions in acid and weakly alkaline mediums (pH range of 0-9), however, in strongly alkaline medium they nearly do not dissociate [3]. Therefore, the determining factor in achievement of high gold holding capacity is minimum pH of cyanide solution and capability of ion exchange resin to ion exchange in alkaline medium with pH 10-11. Applied in water processing conventional weakly basic anion exchange resins with tertiary amine groups are hardly suitable for gold extraction from solutions with pH > 10.0 due to low gold holding capacity under such conditions, and the proposed techniques of decrease in pH of process solutions to pH 7-9 are not maintainable (acidifying) and lead to evolution of toxic hydrocyanic acid (HCN). The main reason of failures to apply weakly basic anion exchange resins in this case is that the commercial weakly basic anion exchange resins have low values of pKa<8 (negative logarithm of protonation constant), thus, they are not suitable as anion exchange resins in cyanide solutions with pH > 10.0.

Anion exchange capability of weakly basic anion exchange resins strongly depends on pKa of amine groups and pH of cyanide solution. It is known that at pH pH < pKa -2 there exists complete anion exchange function of weakly basic anion exchange resins, and at pH > pKa +2 the anion exchange properties are lost. In order to extract gold from cyanide solutions with pH=10-11 weakly basic anion exchange resins are required with pKa of 11 and higher [3].

Weakly basic anion exchange resins on the basis of acrylonitrile (AN) sorbs gold more efficiently in the form of $Au(CN)_2^-$ from cyanide solutions with pH=10 - 11, that is, they have higher pKa values of active amine groups.

As basic sorbent for production of readily recoverable anion exchange resin for extraction of gold we selected previously developed for water processing polyfunctional anion exchange resin, known as Rossion-25 [4-6]. This sorbent based on porous copolymer of acrylonitrile (AN) and divinyl benzene is characterized by simplicity of synthesis, high total and dynamic capacity (6.5 mg-eqv/g and 2400 mg-eqv/l, respectively), mechanical and osmotic strength. Theoretical capacity of sorbents on the basis of acrylonitrile is 10.8 mg-eqv/g at complete conversion of nitrile groups upon amination by diethylene triamine. This is a very high value, unreachable for styrene-divinyl benzene resins with higher molecular weight of polymer elementary unit.

In order to optimize sorption/desorption properties of basic anion exchange resin with respect to gold extraction we developed a method which provides required positions of functional groups in polymer matrix by introduction of additional inert so called "ballast" component, styrene in this case, which does not participate in sorption processes. It is established experimentally (see Table 1) that for sorption of gold the optimum content of styrene in terpolymer is 50%. It is obvious that decrease in content of AN in the matrix upon addition of styrene decreases total exchange capacity of the sorbent. However, at such high capacity of "basic" sorbent and the fact that upon sorption of gold from actual solutions its content in sorbents does not exceed 20mg/g (0.1 mg-eqv/g), this is not significant.

In addition, existence of styrene in the matrix creates some additional advantages which improve maintainability and cost efficiency of both sorbent and synthesis, namely:

- High strength (the matrix composition is close to that of ABS);
- No AN homopolymer in recycled diethylene triamine applied upon amination;
- Porous structure improving selectivity of the sorbent;
- Possibility to apply saltless dispersion mediums upon copolymerization with simultaneous obtaining of coarse granules of copolymer, which creates difficulties upon granule polymerization of acrylonitrile.

EXPERIMENTAL

The synthesis of anion exchange resin was performed involving the following basic reagents: acrylonitrile, produced by OOO Saratovorgsintez, Standard GOST 11097-86, 99% of main substance; divinyl benzene (DVB), produced by PO TOKEM (Kemerovo), Specifications TU 2414-002-05415812801, 63% of main substance, ethylstyrene (ES) 36%; benzoyl peroxide, Specifications TU 2417-006-51764779-2007, diethylene triamine, Specifications TU 6-02-914-86, 95% of main substance. The synthesis was performed initially in laboratory glass reaction vessels with the capacity of 0.5 l, and then in steel enameled apparatuses with the capacity of 100 l.

The developed method of production of anion exchange resin is as follows: at first porous terpolymer of acrylonitrile, divinyl benzene and styrene is synthesized, and then ammonolysis of nitrile group of polyacrylate polymer matrix is performed by diethylene triamine [7-10]. The obtained anion exchange resin contains weakly basic primary, secondary and tertiary (imidazoline) amine functional groups, which are sterically separated by styrene fragments. The procedure of synthesis and exact compositions of polymerized mixes are described in details elsewhere [6].

Sorption properties of anion exchange resins were det4ermined using reference solution imitating commercial cyanide-alkaline solutions of the following composition, mg/l: Au 4.3; Fe 9.6; Cu 10.8; Zn 8.8; Ni 2.4; NaCN 400; pH 10.5.

Samples of anion exchange resins in S1 form were placed into reference solution at the ratio of anion exchange resin : solution = 1 : 5000 for 24 hours with mechanical agitation at ambient temperature. Saturated samples were removed from the solution, washed in water, dried to constant weight and, after wet combustion, the contents of gold and metallic impurities were determine by atomic absorption.

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RESULTS AND DISCUSSION

Tests results of the obtained samples are summarized in Table 1.

Maximum values of holding capacity and selectivity are observed in sample No. 5 at styrene content of 50 wt %. The holding capacity and selectivity of sample No. 5 are nearly identical to those of commercial analog, PuroGold S 992.

Recovery of saturated sorbents was performed by their treatment by desorbing alkaline-cyanide solution under static conditions. Samples of sorbents, saturated upon sorption from gold containing reference solution, with the weight of 1 g were placed into solution of the following composition, g/l: NaOH 10; NaCN 50, at the ratio of sorbent : solution = 1: 500. The process duration was 6 hours at 60°C. After termination of desorption, washing with water, drying and wet combustion the residual content of gold and metallic impurities was determined by atomic absorption.

Results of comparative desorption tests are summarized in Table 2. Maximum desorption of gold and impurities, equaling to 96% and 92%, respectively, is observed in Rossion-15 sorbent with styrene content of 50%. The properties of commercial analog, PuroGold S 992, are the same. From AM-2B anion exchange resin under the same conditions gold is extracted only by 4%.

Table 1. Comparative properties of capacity and selectivity with respect to gold of experimental and commercial anion exchange resins

Sample No.	Copolymer composition, wt %				Gold holding capacity		Impurity holding capacity, mg/g	Selectivity to gold
	AN	DVB	ES	Styrene	mg/g	mg/ml		
1	75.0	15	10	-	2.03	0.73	6.16	0.33
2	45.0	21	14	20	3.92	1.45	5.60	0.70
3	45.0	15	10	30	4.20	1.63	3.58	1.17
4	40.0	15	10	35	4.61	1.77	3.29	1.34
5	33.3	10	6.6	50	5.23	1.96	2.44	2.14
6	23.3	10	6.6	60	4.12	1.53	2.62	1.57
AM-2B	-	8	5	87	7.5	2.34	18.3	0.41
PuroGold	-	-	-	-	5.20	1.81	2.71	1.92

Table 2. Desorption of gold and metallic impurities from saturated ion exchange resins by alkaline cyanide solutions

Property	Sorbent				
	AM-2B	PuroGold S 992	Rossion-15 styrene content in copolymer, wt %		
			20	35	50
Gold content in saturated ion exchange resins, mg/g	7.50	5.20	3.92	4.61	5.23
Content of metallic impurities in ion exchange resins, mg/g	18.30	2.71	5.60	3.29	2.44
Residual gold content in ion exchange resins after desorption, mg/g	7.20	0.22	0.59	0.46	0.22 (0.13)*
Residual content of metallic impurities in ion exchange resins after desorption, mg/g	6.70	0.24	1.01	0.32	0.19
Desorption extent of gold, %	4	96	85	91	96 (98)
Desorption extent of metallic impurities, %	63	91	82	90	92

*In parenthesis: values for Rossion-15A alkylated sorbent

The desorption rate of gold can be increased from 96% to 99%, and the residual gold content in sorbent can be decreased nearly twice, to 0.083--0,130 mg/g, if minor amount of carboxyl groups is added into the matrix by partial alkylation of primary amine groups of anion exchange resin by monochloroacetic acid (MCA).

This does not influence significantly on composition of strippant and performances of the process, however, if more complete extraction of gold and two-fold reduction of its content in sorption raffinates are required, it is possible to apply this modification of anion exchange resin. Morevoer, the alkylation process is simple and low-waste [11].

The optimum content of MCA for alkylation, which actually does not decrease the holding capacity of sorbent, is 10 mole % of content of primary amine groups. The chemistry of the process is as follows:
$\mathrm{Res} - \mathrm{C}(=\mathrm{NH})\mathrm{N}(C_2H_4NH_2)_2 + 2ClCH_2COONa \rightarrow \mathrm{Res} - \mathrm{C}(=\mathrm{NH})\mathrm{N}[\mathrm{C}_2H_4NH(CH_2COONa)_2]_2$+2HCl,
where Res is the polymer.

Variation of functional composition of Rossion-15 anion exchange resin, containing 50% of styrene in the matrix, after partial alkylation is summarized in Table 3. The content of primary amine groups decreased by 11%, and that of secondary groups nearly doubled.

Upon desorption of gold from Rossion-15A alkylated sorbent in dynamic mode with supply of eluent of previous composition at the flow rate of 2 vol/vol per hour the residual content of gold in Rossion-15A and PuroGold S 992 anion exchange resins is 0.083 mg/g and 0.176 mg/g, respectively. The desorption rate of gold under these conditions is 98.7% and 96.8%, respectively.

The influence of pH of cyanide gold-containing solution on the holding capacity of the sorbents is summarized in Table 4. It is obvious that the sorption properties of both weakly basic sorbents in the pH range of 8-11 are nearly the same.

Table 3. Functional composition of anion exchange resins

Type of amine groups	Content of amine groups, % of cumulative value			
	Rossion-15, 50% styrene	Rossion-15A, 50% styrene, alkylated	PuroGold S 992	AM-2B
primary	65.5	54.2	2.4	-
secondary	13.5	25.6	59.0	-
tertiary	21.0	20.2	9.9	72
quaternary	-	-	8.7	28

Table 4. Sorbent capacity as a function of pH at 5 mg/l of gold content in solution; NaCN – 400 mg/l

Sorbent	Gold holding capacity, mg/g at pH:					
	8.0	9.0	10.0	10.3	10.5	10.8
Rossion-15	8.32	7.02	6.11	5.51	5.23	3.92
PuroGold S 992	8.12	7.04	6.14	5.45	5.20	4.07

Upon scaling up of the synthesis of Rossion-15A readily recoverable anion exchange resin a pilot batch of anion exchange resin was produced in regular steel enameled reactor with the capacity of 100 l. The scaling coefficient is 200. No problems were encountered upon modification of hydrodynamic modes and conditions of heat transfer. The anion exchange resin, obtained under scaled up conditions, had the same sorption properties. The yield of the fraction, Class “A” was 82%. Mechanical impact and abrasion strength of the exchange resin is 99%.

CONCLUSIONS

Synthesis of readily recoverable anion exchange resin with the aim of gold extraction from cyanide mediums has been developed on the basis of acrylonitril–styrene–divinylbenzene terpolymer with subsequent ammonolysis by diethylene triamine. Technological trials demonstrated identity of sorption properties of the obtained anion exchange resin and PuroGold S 992 commercial sorbent. The developed procedure of synthesis is simple and low-waste, the procedure can be readily scaled up. The synthesis is performed with domestic raw stock except for diethylene triamine, which can be obtained from polyethylenepolyamine produced by AO “Uralkhimplast”.

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