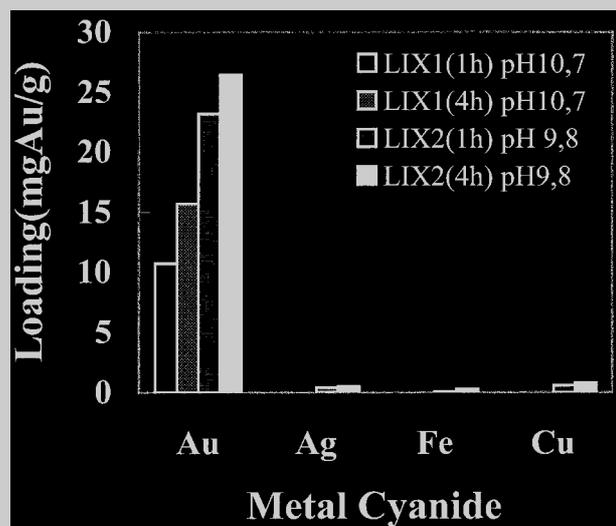


Full Paper: Ion exchange technology is offered as an alternative to activated carbon for gold cyanide recovery. A new type of ion-exchange resin (PS-PIP) incorporating a piperazine group, linked to a styrene-divinylbenzene macroporous network, is described. The extraction of $\text{Au}(\text{CN})_2^-$ and other metal cyanides with the PS-PIP resin involves three modes of metal extraction: the protonated secondary amine groups of the resin (at acidic pH conditions), the free amine groups of the resin (at neutral and basic pH values) and the small portion of the quaternary ammonium groups participate in the gold extraction mechanism. The gold cyanide extraction reaction on the polymeric piperazine was studied by a combination of metal extraction data, from batch experiments, and IR and XPS spectroscopic analysis of the metal loaded polymers. Extraction isotherms of gold cyanide show that gold binding is possible from 40–60 mg Au/g of resin in alkaline solutions, up to 150 mg Au/g of resin in acidic solutions. Efficient stripping of gold from the resin was achieved using ethanol/water solutions of sodium hydroxide, or 0.5 mol/l thiourea in sulfuric acid solutions.



Loading for the different metal cyanide complexes for PS-PIP resin for two mining leaching solutions (S1 and S2).

Ion Exchange Resins for Gold Cyanide Extraction Containing a Piperazine Functionality, 2^a Study of the Gold Extraction Reaction

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Introduction

Hydrometallurgical routes for processing gold minerals are based on the combination of cyanidation with subsequent gold cyanide complex ($\text{Au}(\text{CN})_2^-$) adsorption on activated carbon (AC).^[1–2] Recent research efforts were directed towards substitution of AC by ion exchange resins (IX)^[3–4] in order to solve existing problems associated with the use of activated carbon and aim to: 1) improve the selectivity of gold cyanide recovery; 2) increase loading and stripping efficiencies; and 3) develop integrated processes of leaching and extraction, known as resin-in-leach (RIL) and resin-in-pulp (RIP)

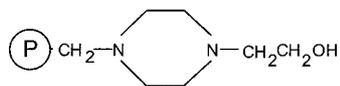
processes.^[5–9] Commercially available resins are unable to compete with activated carbon (AC) due to poor selectivity, mechanical breakdown of the IX beads and complicated regeneration processes. Yet, IX resins offer some chemical advantages over activated carbon and have excellent technical potential for application in gold extraction systems.^[3,5–7] In the above-cited studies, while gold was effectively adsorbed on strong base anion exchange resins, the elution required very strong, and very expansive eluants, such as thiourea, thiocyanate, or zinc cyanide. In comparison, weak base resins have about one-half of the loading capacity of strong base resins, but are readily eluted by high pH solutions.^[10] To increase the capacity of a weak base resin for gold extraction at the

^a Part 1: cf. ref.^[24]

authentic leach solution conditions, it is necessary to increase the pK_a value of the functional amine group on the resin. The requirement for protonation of the weak base resins prior to the interaction with gold cyanide prompted an investigation to understand the factors that influence the basicity of an ion exchanger. In addition to resin acidity, other properties may influence its affinity for gold cyanide, for example, the structure of the ion exchange resin as a complex system. The access of metal anions to the protonated functional groups might be hindered by the number and size of groups attached to the resin matrix, thus resulting in a crowding effect.

Efforts have, therefore, been made to develop resins with high pK_a values to facilitate the extraction of gold at the natural pH of a cyanide leach solution ($\approx 9-10$). New weak base anion-exchange resins, containing primary, secondary and tertiary amine functional groups, were synthesized. Among the attempts reported in the literature the following deserve mentioning: Green et al.^[11-15] in an extensive work on imidazole and imidiazoline resins studied the factors that affect the performance of a set of resins, i. e., basicity and accessibility of the active group; Hodgkin^[16] and Fawell et al.^[17-19] synthesized polydiallylamine based resins (PDAA), Harris et al.^[20] synthesized moderate base polyamine macroporous styrene-divinylbenzene resins from 1,3-diaminopropane or 2,4-diamino-2-methylpentane and chloromethylated styrene-divinylbenzene copolymers with improved capacity for gold loading from cyanide solutions. More recently, the Henkel Co. announced the development of a new resin carrying alkylguanidine functionality^[21] for gold cyanide extraction from cyanide solutions.

The present paper, the second in this series, discusses the properties of a new ion exchange resin based on piperazine functionality for gold cyanide extraction from cyanide solutions. The piperazine resin was prepared by attachment of an ethylhydroxypiperazine group to a polystyrene-divinylbenzene matrix (P) of the following structure and described as PS-PIP:



PS-PIP is synthesized by chloromethylation of aromatic styrene-divinylbenzene (PS-DVB) copolymers (Amberlite XE-305) as described in previous papers.^[22, 23] Details of the synthesis of this resin and the acid-base properties of the piperazine functional groups are published in the first paper.^[24] There it was shown that the acid-base properties of the secondary amine groups of the piperazine polymeric ligand were strongly modified by attachment to the PS-DVB macroporous matrix with an increase in the acidity properties of the piperazine group.

The present paper describes the metal cyanide extraction behavior of the piperazine based PS-DVB macropor-

ous resin (PS-PIP). The extraction and re-extraction mechanisms were determined and the structure of the polymer-bound metal cyanide complexes was elucidated using FTIR and XPS spectroscopy. Description of the extraction processes was achieved by analysis of the equilibrium parameters. Finally the application of the piperazine resin for gold extraction from cyanide solutions was evaluated on different mineral leaching solutions obtained from a Brazilian mineral.

Experimental Part

PS-PIP Resin

The resin (PS-PIP), synthesized as described previously,^[23, 24] incorporates a piperazine group, linked unto a styrene-divinylbenzene macroporous network. The surface area of this resin was determined as $302 \pm 5 \text{ m}^2/\text{g}$ by using the BET method. The resin in the wet form was conditioned by cyclic exhaustion with 1 mol/l HCl and regeneration with 1 mol/l NaOH and finally washed thoroughly with a large volume of distilled water and stored in water. The resin contained 60% water and had 1.94 mmol/g proton capacity by acid base titration. Particle sizes of the functionalized resins ranged from 0.2 to 0.9 mm.

Reagents and Solutions

NaCN solutions were maintained at pH above 11 (by using sodium hydroxide) to avoid hydrogen cyanide (HCN) formation. These solutions were used to dissolve metal cyanide complexes. Stock solutions were prepared by dissolving $\text{KAu}(\text{CN})_2$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{KAg}(\text{CN})_2$ and CuCN (Johnson Matthey and Aldrich, A.R. grade) in NaCN solution. Working standard solutions were prepared by appropriate dilution. Hydrochloric acid, sulfuric acid, sodium chloride, sodium hydroxide, sodium cyanide, thiourea and methanol (Fluka, AR) were used in the preparation of the different solutions. Potassium bromide (Merck, for spectroscopy) was used in the preparation of the pressed disks for FTIR.

Mineral Leaching Solutions

Real cyanide leach liquors were obtained by leaching a gold mineral ore (gravimetrically concentrated sample) from Brazil. The gold ore sample was crushed to 100% passing 100 mesh ($<0.149 \text{ mm}$). Two different types of leach solutions were used, a filtered leaching solution (LIX1), and a clarified leaching solution (LIX2), obtained after precipitation of the colloidal phase of the solution by acidification of the solution (pH3-4) and subsequent addition of CaO to increase the pH to values of around 9-10. The composition of both LIX1 and LIX2 leaching solutions are shown in Table 1.

Experimental Gold Cyanide Extraction Procedures

Sorption and Stripping Experiments

For measurement of equilibrium sorption, small-scale dynamic contacts between the resin and metal cyanide complexes were effected. Resin samples between 0.05-0.20 g

Table 1. Compositions of the mineral leaching solutions.

Metal	Filtered solution (S1)	Clarified solution (S2)
	pH=11, [CN ⁻]= 200 ppm	pH=10, [CN ⁻] < 10 ppm
	$\frac{[M]}{\text{mg/l}}$	$\frac{[M]}{\text{mg/l}}$
Gold (Au)	38.1	30.7
Silver (Ag)	2.0	1.7
Copper (Cu)	2.0	2.4
Iron (Fe)	87.3	3.7

were mixed mechanically in special glass-stoppered tubes with an aqueous solution (20–250 ml) until equilibrium was achieved. The composition of the aqueous solutions varied depending on the nature of the experiment. After phase separation by high-speed centrifugation, the equilibrium pH was measured using a Methrom AG 9100 combined electrode connected to a CRISON digital pH-meter. Metal content in both phases was determined by atomic adsorption spectrophotometry (Varian 680 with air-acetylene flame) or inductively coupled plasma spectrophotometry (ICP) (SpectroFlame, Kleve, Germany) depending on solution composition.

The extent of sorption was calculated from the residual concentration of the metal cyanide complexes in the equilibrated solution. A range of pH (2 to 14) and gold cyanide concentrations (1 to 500 mg · dm⁻³) were employed.

For the stripping efficiency measurements, similar batch experiments using the gold loaded resin and various stripping solutions were conducted. Samples employing 0.05–0.20 g of the resin were mixed mechanically in special glass-stoppered tubes with a stripping solution (5–10 ml) until equilibrium was achieved. Stripping solutions of NaOH (40 g/l), NaOH (40 g/l) in ethanol (50% v/v), NaCN (5 g/l) and thiourea (1 g/l) in H₂SO₄ (0.5 M) were used. The metal content in both phases was determined as described previously.

Column Experiments

Known amounts of swollen resins were slurry-packed in an Omnifit borosilicate glass column (0.5 mm I.D. and 20 mm length) fitted with porous 25-micron polyethylene frits and Teflon end pieces. A peristaltic pump at the column entrance delivered solutions at a constant flow rate of 0.5 to 1 ml/min. Metal cyanides extraction histories were determined by following the change in concentration of samples at the column exit. After each extraction experiment, the flow of the metal solution was stopped and the resin washed successively with water and then washed with the stripping solution at a flow rate of 0.5 ml/min.

FTIR Analysis of PS-PIP Resins

Piperazine and PS-PIP resin samples were equilibrated with aqueous solutions of different pH values (2, 7.6, 11.5 and 14) and with gold cyanide solutions at different pH values (2, 7.6, 11.5, 14). FTIR spectra were recorded on dry samples with a BOMEM MB120 Fourier Transform Infrared Spectrometer (4000–700 cm⁻¹). 32 interferograms were scanned at

2 cm⁻² resolution. Potassium bromide was used for the preparation of the pressed disks for FTIR.

X-Ray Photoelectron Spectroscopy

Spectra were recorded using a vacuum Generators Escalab Mk II X-ray photoelectron spectrometer with a base pressure of <10⁻¹⁰ bar and calibrated for both absolute binding energy (BE) and linearity, using the Cu(2p_{3/2}) (932.6 eV), Au(4f_{7/2}) (84.0 eV) and Ag(3d_{5/2}) (368.1 eV) photoelectron peaks as described elsewhere.^[24]

Samples of the dried resins, in bead form, were cooled to ca. 150 K (to minimize any thermally induced radiation damage) before excitation with Mg K_α X-rays, operated at a power of 300 W. The C(1s) photoelectron peak BE of the PS-PIP resin backbone was adjusted to the 284.6 eV^[19,24,25] C(1s) BE value for polyethylene. From a photoelectron spectroscopic viewpoint, this resin consists of carbon atoms in the general groupings of phenylene, methyl, methylene and methylidyne. Although the use of polyethylene as a BE reference applies strictly only to the methylene carbons, any aliphatic carbon (provided it is not attached to a highly electronegative or electropositive group) will have the same BE within experimental error. Interestingly, the same holds true in simple aromatic systems, as benzene carbons have C(1s) BE reported values of 284.8^[26] to 284.9 eV.^[27] Ring substituents may however have a major effect, as for example in methyl benzene: the methyl C(1s) BE is at 284.7 eV, whereas the average ring C(1s) BE value is at 285.2 eV.

Results and Discussion

Gold Cyanide Adsorption Isotherms

According to previous adsorption studies on weak base ion exchange resins,^[13–24] the effect of pH on the extent of gold cyanide adsorption was significant, especially when moving from acidic to basic values. Gold cyanide loading capacities of PS-PIP resin were measured by batch experiments at different pH levels of the aqueous cyanide solution. Gold cyanide equilibrium isotherms (Figure 1) show an S-shaped function falling rapidly from 150 mg Au/g resin at pH 2 to 40 mg Au/g resin at pH 10 and maintaining a loading concentration of 20 mg Au/g resin in a highly alkaline solution of 1 M NaOH.

To simulate the pH conditions of the leaching solutions of the resin-in-leach (RIL) or resin-in-pulp (RIP) processes, the adsorption of Au(CN)₂⁻ by the PS-PIP resin was determined at pH 10. The gold cyanide isotherms, determined by a batch equilibrium method from a 100 ppm CN⁻ solution at pH 10 (adjusted by addition of CaO(s)), are plotted in Figure 2. The equilibrium sorption increases proportionally to gold cyanide concentration in the aqueous phase. Loading of 60 mg Au per gram of resin was achieved at the saturation limit (35% of the total ion exchange capacity).

A simple adsorption model was used to describe the data as a first approach approximation. The extraction

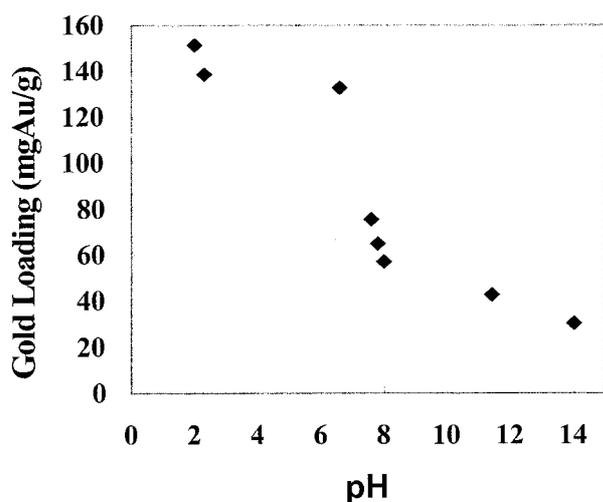


Figure 1. Gold loading (mg Au/g resin) as a function of pH in the aqueous phase. $[\text{Au}(\text{CN})_2^-] = 500$ ppm, phase ratio was 0.2 g resin/20 ml of solution.

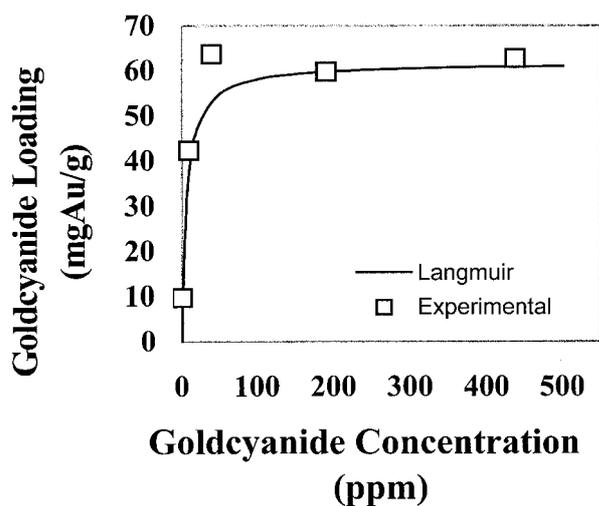


Figure 2. Predicated and experimental gold cyanide loading (mg Au/g resin) as a function of gold cyanide concentration in the aqueous phase for PS-PIP resin (1.94 mmol/g). Phase ratio was 0.2 g resin/20 ml of solution.

isotherm data fits very well into the Langmuir isotherm equation:

$$Y = \frac{K_b Y^+ C}{1 + K_b C} \quad (1)$$

where Y is the equilibrium adsorption (mmol Au/g dry weight resin) and C is the equilibrium sorbate concentration (mmol/l). K_b represents the adsorption binding constant (l/mmol) and Y^+ saturation adsorption capacity (mmolAu/g dry weight resin). Those parameters were determined by the least squares fit of the adsorption data and are shown in Figure 2.

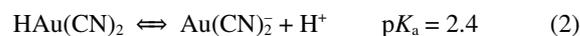
Fitting the Langmuir isotherm implies that the adsorption of gold cyanide is dependent on more than one

adsorption mechanism, probably involving both the protonated and free forms of the tertiary amines of the piperazine groups and also the residual quaternary ammonium groups. This conclusion suggests that further attempts be made to elucidate the adsorption mechanism and to determine the various types of nitrogen functionalities present on the resin.

IR Spectroscopic Characterization of the Loaded PS-PIP Resins

The infrared spectra of the loaded resin samples show a sharp band in the range 2141 to 2157 cm^{-1} , assigned to the CN^- stretching vibration of the aurocyanide complex.^[28] Table 2 shows the frequency changes of various gold loaded samples. A frequency increase from 2142.9 cm^{-1} for the resin loaded at pH 14, to 2156.8 cm^{-1} for the resin loaded at pH 2 is observed. Comparing with potassium salt ($\text{KAu}(\text{CN})_2$),^[29] there is no appreciable change in the frequencies of the resins loaded at basic pHs (12 and 14). This supports the contention that the interaction between the gold complex and the amine groups of the resin is solely an ionic interaction and is attributed to the presence of quaternary ammonium groups on the resin and hence the formation of the gold cyanide complex $[\text{R}_4\text{N}^+\text{Au}(\text{CN})_2^-]$. This reaction was previously described for strong-base anion exchange resins (Dowex A1, IRA900, Dowex XF4149 and IRA 400) (Table 2) and also found in other extractant-gold(I) cyanide systems, such as activated carbon^[29] or in organic solvents.^[30–34]

Changes in the IR frequencies in the acidic range values (2155 cm^{-1} at pH6 and 2157 cm^{-1} at pH2) may be an indication of the existence of interactions of the CN^- group with the free amine groups of the resin or for the protonation of the gold cyanide complex ($\text{Au}(\text{CN})_2^-$). The protonation reaction of this anion is described by the following reaction:^[35]



Accordingly at pH2, in the aqueous phase, the aurocyanide anion is almost 70% in the protonated form ($\text{HAu}(\text{CN})_2$) and hence the extracted gold cyanide in the resin phase is also in the protonated form. This is corroborated by an increase in the frequency of the cyanide ion; from 2142 cm^{-1} for the anionic form ($\text{Au}(\text{CN})_2^-$) to 2157 ($\Delta\nu(\text{CN}^-)$ cm^{-1} for the protonated form). These observations are in agreement with the expected frequencies changes observed for acidic organophosphorus ligands ($\text{RRP}(\text{O})\text{OH}$) adsorbed onto polymeric supports when converted from protonated to ionic form.

Infrared (IR) spectroscopy was used previously to confirm the presence of the $\text{Au}(\text{CN})_2^-$ anion on ion-exchange resins^[19,37–39] and other polymeric materials.^[41] A strong band observed near 2141 cm^{-1} was assigned to the ν_3 CN

Table 2. Compilation of the stretching frequencies of CN⁻ in loaded piperazine samples.

Sample	$\nu(\text{CN}^-)$ cm^{-1}
<i>Salts</i>	
KAu(CN) ₂ (s)	2 140, ^[37] 2 141, ^[29] 2 145 ^[31]
HAu(CN) ₂ (s)	2 212, ^[37] 2 146 ^[29]
AuCN(s) polymeric	2 261, ^[37] 2 239 ^[29]
LAuCN (L = Ph ₃ P)	2 138 ^[41]
LAuCN (L = Et ₃ P)	2 145 ^[42]
<i>Aqueous Solutions</i>	
K ⁺ Au(CN) ₂ ⁻	2 142 ^[37]
H ⁺ Au(CN) ₂ ⁻	2 147 ^[37]
<i>Ion Exchange Resins</i>	
PS-PIP + Au(CN) ₂ ⁻ loaded (pH = 2)	2 156.8 (this work)
PS-PIP + Au(CN) ₂ ⁻ loaded (pH = 7.6)	2 155.0 (this work)
PS-PIP + Au(CN) ₂ ⁻ loaded (pH = 11.5)	2 145.1 (this work)
PS-PIP + Au(CN) ₂ ⁻ loaded (pH = 14)	2 142.9 (this work)
Dowex A1+ Au(CN) ₂ ⁻ loaded (pH = 11)	2 138 ^[37]
IRA 904 Au(CN) ₂ ⁻ loaded (pH = 10)	2 142.4 ^[37]
Dowex XF4149 + Au(CN) ₂ ⁻ loaded (pH = 11)	2 142.2 ^[37]
IRA 400 Au(CN) ₂ ⁻ loaded (pH = 11)	2 142.4 ^[37]
<i>Activated Carbon</i>	
AuCN (s)	2 239 ^[50]
Au(CN) ₂ ⁻	2 140 ^[50]
<i>Organic Solvents</i>	
Tridecylamine/xylene + Au(CN) ₂ ⁻	2 140 ^[34]
Adogen 283/TBP/CCl ₄ + Au(CN) ₂ ⁻ (pH = 8.0)	2 140.1 ^[30]

stretching of the gold complex, whereas the polymeric Au(CN), showing a CN stretching frequency of 2261 cm⁻¹,^[37] very readily distinguished from the Au(CN)₂⁻ complex. Values of 2 138 and 2 146 cm⁻¹ were measured for Et₃PAuCN^[40] and Ph₃PAu(CN).^[41] Simple salts of Au(CN)₂⁻ show a large shift for the CN stretch.^[42] These results suggest that the CN stretch in the IR spectrum is far from being conclusive evidence for the existence of Au(CN)₂⁻ and for providing a definite description of the chemical absorption reactions pertinent to the behavior of PS-PIP resin in the basic range.

The spectra of the sample of pH2 also show two bands in the zone 2700–2200 cm⁻¹, assigned to the N–H asymmetric and symmetric stretching vibrations, of the protonated tertiary N atom of the piperazine resin and thus mark the anion exchange reaction of the gold cyanide complex. The same two bands were obtained for the chlorhydrate of piperazine at pH2. Notably, samples at pH 7.6, 11.5 and 14 did not show this band, indicating that the N₂ (terminal nitrogen of the piperazine group and distal to the back bone) is incompletely protonated. Thus, if N₁ (the vicinal nitrogen of the piperazine group close to the back bone) is not protonated the adsorption of the gold cyanide anion may be by means of a ligand substitution reaction in which one of the cyanide molecules of the complex is substituted by the amine.

XPS Analysis of the Gold Cyanide Loaded PS-PIP Resins

X-ray photoelectron spectroscopy (XPS) is an alternative spectroscopic technique for evaluating adsorption states. This method has proved particularly useful in determining the mechanism of aurocyanide adsorption onto activated carbon (AC) and more recently with ion-exchange resins.^[17–19, 29] This is due to the ability of XPS to establish chemical states from binding energy shifts and stoichiometries from peak intensities.

The marked sensitivity of the weak base piperazine resin N(1s) photoelectron peak to the extent of protonation was shown in the first paper in this series.^[24] The effects of simple alterations in the chemical environment of the amine functional groups were examined by equilibrating the PS-PIP resin in solutions of different pH values. Three different N types were detected; free tertiary amines of the piperazine group (399.7 eV), protonated tertiary amines (401.3 eV) and quaternary ammonium groups (402.3 eV) are all present within the same matrix. Since at pH2 the band is very broad, it implies that both nitrogens (N1, N2) of the piperazine group are only partially protonated as confirmed also by acid-base titration curves.

Adsorption of cyanide complexes onto amine type resins implies that a minimum of three (free amine, protonated amine and quaternary ammonium groups) and perhaps a fourth N(1s) (the cyanide, in addition to the three previous states) may be observed. The appearance of a low binding energy nitrogen at 398.7 eV attributed to cyanide (398.6 eV) was observed in activated carbon,^[45] Figure 3 shows the N(1s) photoelectron peaks shifting to lower binding energy value upon increasing pH. Deconvolution of the different XPS spectra for the N(1s) allows us to determine the area of the different N present in the loaded samples at different pH values and the results are collected in Figure 4. The deconvolution model was chosen in consideration of the fact that four different nitrogen types could be present on the resin, based on previous citations of XPS analysis of nitrogen containing ion exchange resins.^[17, 18, 43–45] Although other more simple (2 or 3 nitrogen types) or more complex (5 nitrogen types) models were evaluated, the model giving the best description of the adsorption behavior was chosen and presented in this paper.

The peak deconvolution shows the decrease of the N(1s) peak in the CN⁻ anion proportionally to increase in pH and decrease in gold loadings and concurrent disappearance of the protonated amine group peak upon pH shift from the acidic to the basic side. For pH14 samples the presence of both the CN⁻ and the quaternary ammonium groups is detected. Yet this peak decreases due to the reduction of the gold content inside the resin phase. The relative areas of the N(1s) peaks of the different samples are collected and shown in Table 3.

Table 3. Peak areas under the N(1s) and Au(4f) photoelectron peaks in Figure 4 for the gold loaded PS-PIP resins at different pH values.

Sample	N of CN ⁻ N(1s) 398.7 eV	N(1,2) of (NR ₃) N(1s) 399.7 eV	N(1,2) (NR ₃ H ⁺) N(1s) 401.3 eV	N (NR ₄ ⁺) N(1s) 402.3 eV	Au of Au(CN) ₂ ⁻ Au(4f) 85.04 eV
Resin loaded (pH = 2)	4485 ± 115	1561 ± 115	2819 ± 120	d. ^{a)}	3541 ± 123
Resin loaded (pH = 7.6)	7607 ± 142	3348 ± 156	1569 ± 125	d.	3358 ± 89
Resin loaded (pH = 11.5)	5576 ± 165	4688 ± 210	n. d. ^{b)}	640 ± 100	2386 ± 79
Resin loaded (pH = 14)	5573 ± 232	5656 ± 190	n. d.	769 ± 121	1445 ± 89

^{a)} d. = detected peak with an area <5% of the total area.

^{b)} n. d. = not detected peak.

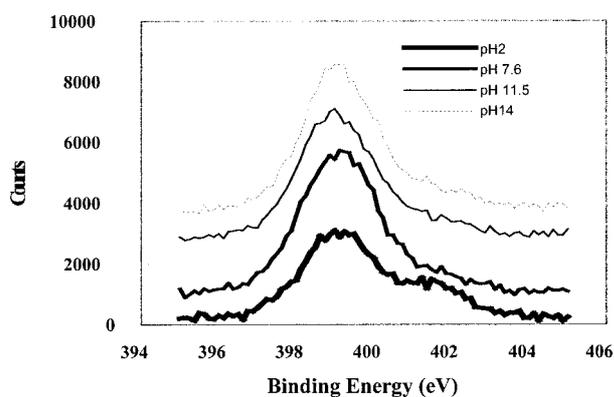


Figure 3. The effect of pH (2, 7.6, 11.5, 14) on the piperazine amine N(1s) photoelectron peak of the gold loaded PS-PIP resin. Protonation of the amine produces a shift to higher binding energy. Additionally the appearance of a new peak at lower energies than the tertiary amine nitrogen was observed.

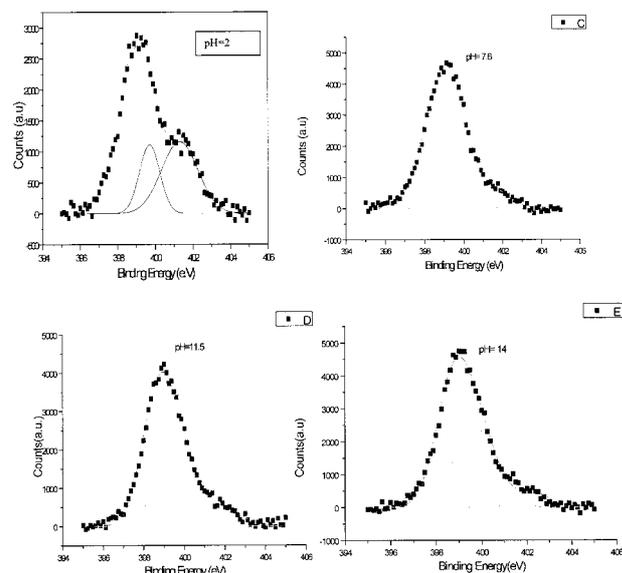


Figure 4. Deconvolution of N(1s) peaks of piperazine resins at pH 2, 7.6, 11.5 and 14.

Figure 5 shows the Au(4f) and N(1s) photoelectron binding energies for the loaded resins at various pH solutions. The Au(4f_{7/2}) BE value for gold adsorbed on the

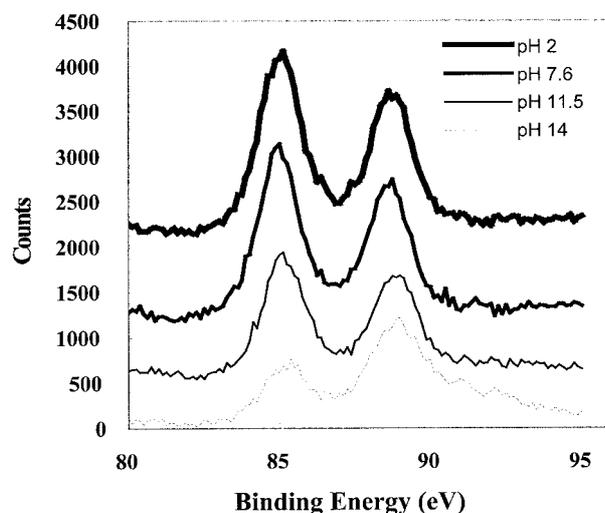


Figure 5. The effect of pH on gold loaded piperazine Au(4f) and N(1s) photoelectron peak. Binding energies.

Table 4. Binding energy for gold and various gold compounds.

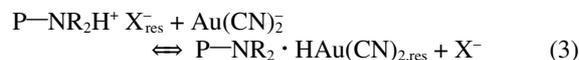
Compound	Binding energy Au 4f _{7/2} (±0.2 eV)	Oxidation state of Au	Ref.
Au(s)	83.8	0	[45]
AuCN(s)	85.0	+I	[52, 53]
KAu(CN) ₂ (s)	84.9	+I	[45] ^{a)}
AuCl(s)	86.4	+I	[45]
Au ₂ O ₃ (s)	85.7	+III	[45]
Au[CS(NH ₂) ₂] ₂ ⁺	84.4	+I	[45]

^{a)} Relative to hydrocarbon (C 1s) at 284.6 eV.

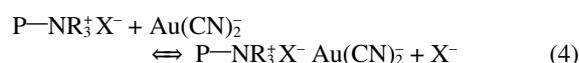
PS-PIP resin is 85.1 ± 0.1 eV. The oxidation state of gold is easily deduced by comparison with the BEs of the Au(I) standards in Table 4 and in previously published observations.^[19, 46–47] For the formal loss of each electron, there is almost exactly a 1.0 eV increase in the BE from that of Au(0) at 84.0 eV. Gold appears on the PS-PIP resin as Au(I) with some charge donation away from the gold atom.

Gold Cyanide Adsorption Mechanism on PS-PIP Resins

Taking into account the apparent acidity constant of the piperazine group ($pK_{H(a)} = 7.1 \pm 0.1$) and the IR and XPS results, the following reaction describes the gold cyanide adsorption process:

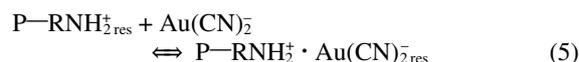


In addition, an anion exchange reaction takes place – over the whole pH range – due to the presence of residual quaternary ammonium groups formed during the synthesis of the resin:

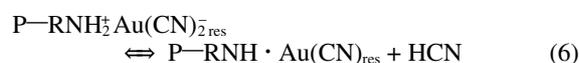


Previous studies on polyalkylamine (PDDA) reported anomalous behavior of weak base resins^[16, 17–19] and found two mechanisms governing the adsorption of aurocyanide onto PDDA containing resins depending on the extent of protonation of the resin as follows:

a) anion exchange reaction



b) ligand exchange reaction



where P represents the polymeric matrix of the resin.

In the present study, $Au(CN)_2^-$ was not detected in the resin phase. The adsorption behavior observed at higher pH values in the presence of quaternary ammonium groups could not be fully explained by FTIR or XPS data. Identical behavior was observed for polyamide moderate base resins, containing 16% quaternary amine groups.^[20] Laskorin^[46] found that salt splitting or strong base character increased gold loadings at higher pH values and several weak base resins possess a significant number of quaternary ammonium groups, the accidental result of side reactions during the manufacturing process.

Stripping of PS-PIP Resins

The loaded phases obtained in the adsorption experiments were used for the study of the stripping of $Au(CN)_2^-$. Taking into account different possible adsorption mechanisms, different complementary types of eluting solutions were used: aqueous solutions of NaOH, NaCN and thiourea/ H_2SO_4 and ethanol/water NaOH solutions. The elution data shows that aqueous solutions of NaOH and NaCN gave partial recoveries (50–60%) while thiourea and ethanolic solutions of NaOH achieved quantitative recoveries of $Au(CN)_2^-$ from the resin phase.

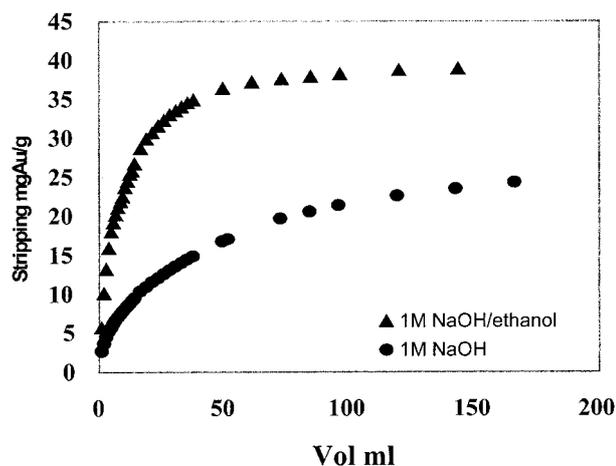
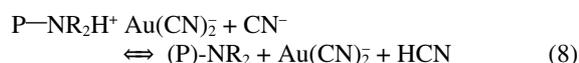
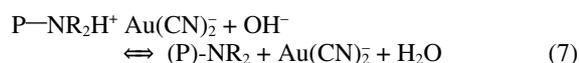


Figure 6. Stripping efficiency of gold cyanide from PS-PIP resins.

The elution behavior may be understood taking into account the nature of the eluant and the gold adsorption mechanism. With aqueous NaOH and NaCN solutions having basic properties the deprotonation of the tertiary amine group is the prime driving force for the elution:

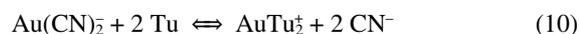


whereas an anion-exchange reaction explains the elution of the quaternary ammonium groups:

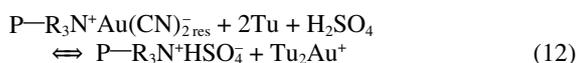
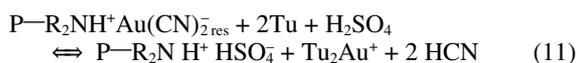


Quantitative elution of gold cyanide from the resin was achieved in the case of aqueous/ethanol NaOH solutions. Figure 6 shows the elution efficiency as a function of the stripping volume in a column experiment. Past experience of gold cyanide desorption from activated carbon^[47–49] showed the rate of elution enhanced in the presence of polar solvents, such as acetonitrile, acetone, methanol and ethanol. The significant enhancement of the rate of elution was attributed to an increased activity of the cyanide ion and a decreased activity of the aurocyanide ion, in polar solvents, as compared with water.

In the case of thiourea (Tu), a ligand with strong complexing properties for many heavy, noble and precious metals,^[4] a substitution reaction takes place, changing the charge of the complex:



The elution of the absorbed gold is by the following reactions:



where thiourea (Tu): $\text{CS}(\text{NH}_2)_2$.

XPS Studies on Eluted Resin Samples

Most of the loaded gold was readily eluted by treatment with ethanolic solutions of sodium hydroxide. Atomic absorption analysis of the eluates indicated that approximately $98 \pm 3\%$ of the initial gold on the resin was removed. Examination of the XPS spectra (Figure 7) showed an absence of the gold(I) peak on the eluted PS-PIP resin and in the totally eluted sample (NaOH in ethanol) and a presence of a gold(I) peak in the sample partially eluted with NaOH. A shift of the Au $4f_{7/2}$ peak to higher binding energies of 88.6 eV was observed. This shift indicates that residual gold held in the PS-PIP resin matrix is not in the reduced form of Au(0). In many previous cases where partial elution of gold cyanide took place (activated carbon^[50] and ion exchange resins^[17–19]) a Au $4f_{7/2}$ peak around 84.0 eV was observed. We did not observe any peak close to this value in either sample.

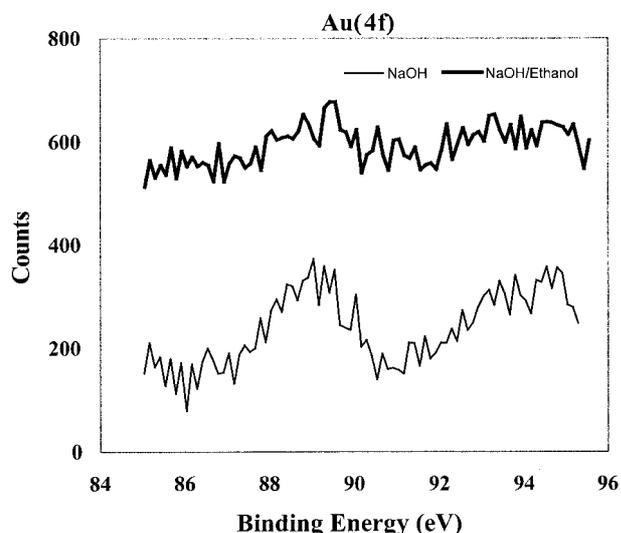


Figure 7. The effect of elution on the Au(4f) photoelectron peak on loaded and unloaded samples of piperazine resin.

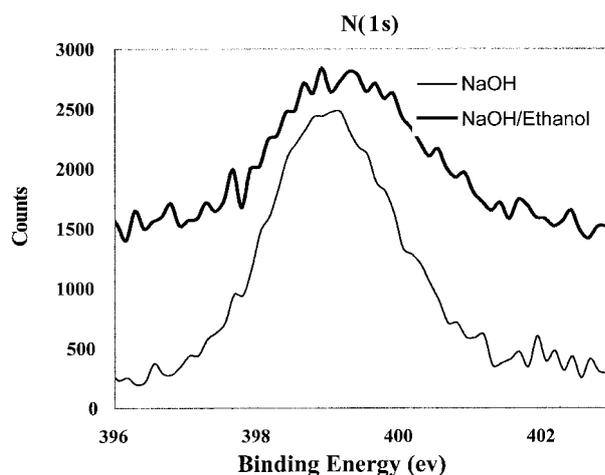


Figure 8. The effect of elution on the N(1s) photoelectron peak on loaded and unloaded samples of piperazine resin.

Further analysis of the N(1s) photoelectron peaks (Figure 8) of both samples did not show the N(1s) cyanide at 398.7 eV in the sample eluted with ethanolic solutions although the peak at 399.7 eV was slightly shifted to 399.5 eV. The deconvolution of the peak detected the presence of the N(1s) of both free tertiary amine groups (399.7 eV) and the cyanide anion of the gold complex (this is contrary to the case of the partially eluted aqueous NaOH sample). In both cases the N(1s) peak of the resin-bound small fraction of quaternary ammonium groups (402.3 eV) was not detected. The partially eluted resin sample shows the presence of the N(1s) peak of the cyanide molecule at 398.6 and this was deconvoluted in Figure 9. Table 5 shows a collection of the deconvolution distribution areas for both samples.

Adsorption Efficiency and Selectivity of PS-PIP for Gold Adsorption from Mine Cyanide Solutions

The PS-PIP resin's adsorption efficiency and selectivity for the extraction of $\text{Au}(\text{CN})_2^-$ and other metal cyanides complexes from two gold ore mining leaching solutions LIX1 and LIX2 (see *Experimental Part*) at different leaching times (2 and 4 h) was evaluated. Loading of metal cyanides is shown in Figure 10, and values ranging from 5–30 were obtained, similar to those achieved with activated carbon.^[44] Figure 11 shows the metal adsorption

Table 5. Peak areas under the N(1s) and Au(4f) photoelectron peaks in Figure 8 and 9 for the gold loaded PS-PIP resins at different pH values.

Sample	N of CN^- N(1s) 398.7 eV	N(1,2) NR_3 N(1s) 399.5 eV	N(1,2) NR_3H^+ N(1s) 401.3 eV	N (NR_4^+) N(1s) 402.3 eV	$\text{Au}(\text{CN})_2^-$ Au(4f) 85.04 eV
Resin eluted NaOH (60%)	2932 ± 78	1756 ± 81	n.d. ^{a)}	d.	n.d.
Resin eluted NaOH/ethanol (98%)	d. ^{b)}	3072 ± 115	n.d.	d.	1230 ± 81

a) n. d. = not detected peak.

b) d. = detected peak with an area <5% of the total area.

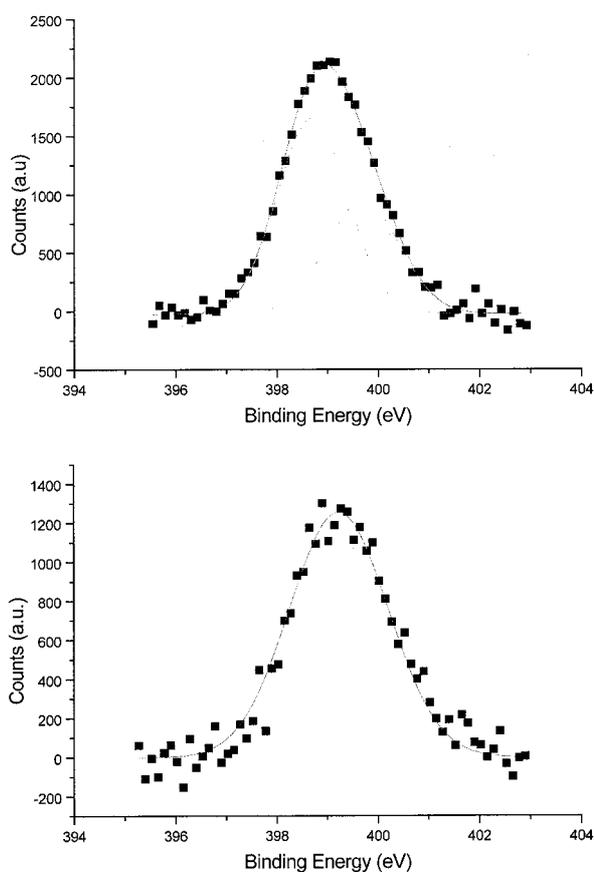


Figure 9. Deconvolution of the 398.6 eV peak shown in Figure 8.

percentages for different metal cyanide loading solutions for the PS-PIP resin. As a general trend, the resin shows that the adsorption efficiency increases as the metal cyanide content increases and as the pH of the leachate decreases.

Besides the ability to absorb gold at the mineral leaching operating pH, the selectivity of the resin for the gold cyanide complex must be high. $K_{S(Au)}$ was calculated by using the following equation:

$$K_{S(Au)} = \frac{Y_{Au} X_{Me}}{Y_{Me} X_{Au}} \quad (13)$$

where Y and X represent the concentration of the metal cyanide in the resin and aqueous phase, respectively (in mg/g).

The selectivity factors ($K_{S(Au/Y)}$) for this set of metal cyanides for the PS-PIP resin calculated were 5 (Au/Ag), 6 (Au/Cu) and 27 (Au/Fe) and comparable with those measured with Hypersol Macronet MN300^[39] resin containing a mixture of tertiary and quaternary ammonium groups: 13 (Au/Ag), 16 (Au/Cu) and 200 (Au/Fe).

The selectivity order for both resins may be arranged as follows:

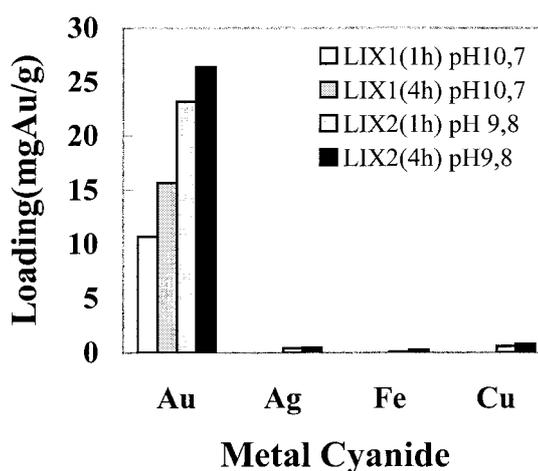


Figure 10. Loading for the different metal cyanide complexes for PS-PIP resin for two mining leaching solutions (S1 and S2).

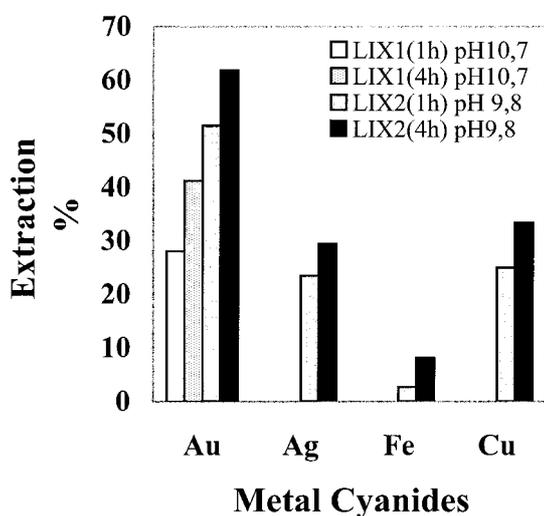


Figure 11. Extraction percentages for the different metal cyanide complexes for PS-PIP resin for two mining leaching solutions S1 and S2 (composition in Table 2).

The hydrophilicity of the polymer matrix and the ionic density (number of ionic groups per unit volume) play an important role in determining the selectivity characteristics of a resin. Ion-water interactions are stronger in the aqueous phase than in the resin phase, for the simple reason that more free water is available for solvation in the aqueous phase, the ions with the greatest ionic charge tend to have lower adsorption onto the resin phase. In the resin phase the low degree of hydrophilicity and low ionic density favors gold and silver and increases the selectivity for those metals over iron and copper.

Conclusions

The typical S-shape function for gold cyanide adsorption supports the classical ion exchange mechanism of a weak base resin, with a decreased adsorption upon the deprotonation.

nation of the N of the tertiary group at pH values between 6 and 8. At higher pH values (pH9 to 14) the resin shows a constant adsorption trend, independent of the pH of the aqueous phase, typically to the adsorption patterns of quaternary ammonium type resins.

At basic pH values it was demonstrated that gold cyanide is absorbed by an ion-exchange process and it is fixed as an anionic species with a 2141 cm^{-1} frequency, typical for the CN molecule. At acidic pH values the absorbed gold cyanide complex exists on the resin as a protonated species (HAuCN_2) as indicated by the frequency shift of the CN^- to 2158 cm^{-1} . This effect starts to show from around pH6, at which the tertiary amine group is completely protonated.

XPS analyses of the different gold loaded resin samples were deconvoluted and four different types of nitrogens were detected, a fourth new peak for N(1s) was detected at 398.7 (in addition to the first three reported when describing the acid-base properties of the piperazine) and is due to the nitrogen of the CN anion, present on the absorbed complex. The Au(4f) peak of the Au atom of the gold cyanide complex was also detected at 85.04 eV. The variation of the normalized areas of the N(1s) of the cyanide groups at 398.7 eV and the Au(4f) of the gold atom of the complex does not remain constant over the pH range evaluated (2 to 14) and it was noted that the normalized (N/Au) ratio did not follow a defined trend, due to the existence of varying adsorption mechanisms in the varying pH ranges.

The PS-PIP resin with a weak base functionality applied to the adsorption of gold cyanide from cyanide media shows promising properties in terms of achieving high gold loadings of 150 mg/g resin at low pH values, however, at basic pH values medium loading capacities of 60 mg/g were achieved, closer to those expected for the use of this resin under normal conditions of resin-in-leach or resin-in-pulp operations at pHs between 8 and 10. Stripping of the gold cyanide complex off the resin was achieved efficiently by using sodium hydroxide in ethanol/water.

The selectivity of the PS-PIP resin for gold follows charge/size considerations and hydration effects. Large size anions having a small charge density are more compatible with the resin. The weakly hydrated aurocyanide anion is adsorbed to a greater extent than the smaller size argentocyanide anion.

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