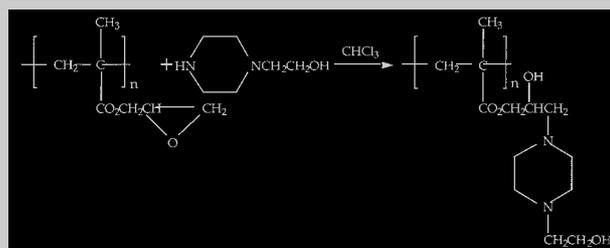


Full Paper: The synthesis of two types of metal-chelating resins incorporating gold-specific piperazine groups is described. PS-PIP is a styrene-divinylbenzene macroporous network. MC-PIP is a (glycidyl methacrylate)-*co*-(ethylene dimethacrylate) network. The nominal functional group concentrations are 1.84 mmol/g for PS-PIP and 1.14 mmol/g for MC-PIP. The proton exchange capacity is 1.95 mmol/g for PS-PIP and 0.91 mmol/g for MC-PIP. Accurate titration curves were used to determine pK_a values ($pK_H = 7.05 \pm 0.12$). XPS analyses of PS-PIP resin were followed as a function of pH (cf. Fig. 8) demonstrating that the protonation of the amine is observable by a shift in binding energy of the N(1s) peak (± 1.6 eV) moving from tertiary amine form (N(1s) 399.7 eV) to the protonated tertiary amine form (N(1s) 401.3 eV). Additionally, the presence of quaternary ammonium groups was detected at a N(1s) peak at 402.3 eV (cf. Fig. 9). Metal extraction from cyanide solutions, including Brazilian mine leach solution, showed considerable preference for gold (cf. Fig. 11–12). The piperazine resins extract gold

via two mechanisms: (a) ligand substitution reactions at $pH > 7.05$ ($pK_{H(a)}$) or (b) anion exchange reactions via the quaternary ammonium groups at high pH values. Extraction profiles were S-shaped (cf. Fig. 10) with 50% extraction ability at pH 8.0. Cyclic experiments involving extraction, elution, regeneration and recomplexation (cf. Tab. 6 and 7) showed the ability of MC-PIP to perform consistently at high extraction efficiencies from pH 8.6.



Synthetic route of MC-PIP resin.

Ion exchange resins for gold cyanide extraction containing a piperazine functionality, 1

Synthesis and physico-chemical properties

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Introduction

The history of applying ion exchange resins (IX) technology in the processing of gold cyanide containing alkaline liquors dates back to the earliest 1950's – the period during which the zinc-dust precipitation method was the industry standard. Since then, there have been sporadic bursts of activity in a number of laboratories around the world.^[1] Recently, however, an increasing number of studies have considered IX as a potential alternative to the well-established processes of activated carbon adsorption and zinc-dust precipitation.^[2,3] Commercially available resins were unable to compete with activated carbon (AC) due to poor selectivity, mechanical breakdown of

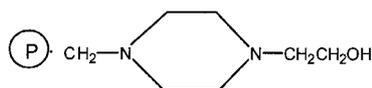
the beads and the requirement for complex elution and regeneration processes following different routes than those used with AC. Yet, IX resins offer some chemical advantages over activated carbon and have excellent technical potential for application in gold extraction systems.^[4–6]

In these initial attempts, described in the literature, gold was adsorbed and eluted effectively using strong base anion exchange resins.^[5,6] However to overcome the high binding energy of strong base resins for the aurocyanide ion, elution required the use of thiourea, thiocyanate, zinc cyanide, and/or polar solvents. The resin must then be regenerated with acid prior to recycling. This

type of elution/regeneration is complex and expensive. It would be highly desirable to apply weak base resins (WBR) to extract gold, since WBR can be eluted by simply shifting the pH to higher values and reverting the gold cyanide binding reaction. Such weak-base anion exchange resins could be applied if the functional group is protonated. This acid-base equilibrium is readily reversed by altering the solution pH converting the resin back into its free base form at pH values around 6–8. As the cyanide leach streams have pH values of around 10–11 this is simply inadequate. As a result only a small percentage of the amine groups in standard weak base resins are protonated in the leach stream and very low exchange of the aurocyanide occurs. Hence commercially available WBRs were found to possess low gold loading capacity due to those low pK_a values.

Efforts have, therefore, been made to develop resins with high pK_a values to allow the extraction of gold at the natural pH of a cyanide leach solution (≈ 9 –10). New weak base anion-exchange resins, containing primary, secondary and tertiary amine functional groups, have been synthesized for the recovery of gold from cyanide solutions.^[9–17]

This paper describes the synthesis of ion exchange resins that aspires to fulfill the needs expressed. Piperazine, a secondary diamine ligand with a pK_a value of 9.8,^[18] was selected as a candidate for the development of suitable resins for gold cyanide extraction from cyanide solutions by functionalizing macroporous polymeric supports. A similar approach was also followed by Chen and Yuan.^[19] 2-Hydroxyethylpiperazine is an inexpensive commercial chemical that can be readily converted to various functional analogs. First, we synthesized a number of different piperazine extractants^[20] and later covalently linked piperazine groups to macroporous polymeric supports. Two different piperazine-based polymeric resins were synthesized (see Fig. 1 and 2) using a different polymeric matrix (P): polystyrene and polymethacrylate. They were characterized chemically and physically determining their acid-base properties, gold extraction capacity and dependence on pH. The acid-base properties were characterized from titration data and were correlated with IR and XPS studies. Their systematic structure is shown below.



Experimental part

Synthesis of the polystyrene based piperazine resin (PS-PIP)

A mixture of 5.023 g PCH_2Cl , 1-(2'-hydroxyethyl)piperazine (piperazine-ethanol) (7 ml) in $CHCl_3$ (60 ml) was stirred (slowly) for 45 h at r.t. and then boiled for 3 h. After cooling,

the polymer was filtered and washed with $CHCl_3 + CHCl_3$ -MeOH, MeOH, MeOH– H_2O , MeOH– $H_2O + MeOH$, and then the product was dried to obtain white beads (6.56 g (86% conversion), capacity = 1.84 mmol/g Pi groups from weight increase and elemental analysis). Resins containing higher contents of piperazine groups were prepared for performing metal extraction studies by increasing the ratio of piperazine-ethanol to PCH_2Cl . Particle sizes of the functionalized resins ranged from 0.2 to 0.9 mm.

Synthesis of N-benzyl-4-(2-hydroxyethyl)piperazine

A mixture of benzyl chloride (10 ml; 0.087 mol) and piperazine-ethanol (16 ml; 0.13 mol) in $CHCl_3$ (40 ml) was stirred at 5°C during 0.5 h, then at r.t. during 1 h and finally at 65°C overnight. After cooling to r.t. the solution was washed with 5% $NaHCO_3$ and brine, and dried over Na_2SO_4 . The solution was filtered, evaporated and dried over P_2O_5 in vacuum to yield 16.635 g (87%) of product.

TLC ($CHCl_3$:MeOH: $NH_3 = 8:2:0.5$): $R_f = 0.65$.

Synthesis of methacrylate based piperazine resin (MC-PIP)

Poly[(glycidyl methacrylate)-co-(ethylene dimethacrylate)] (G-60, 50 g, ≈ 17.5 mmol glycidyl), which was previously washed with $CHCl_3$ and dried at 45°C in a vacuum oven, was refluxed with piperazine-ethanol (4.53 g, 35 mmol) in $CHCl_3$ (dried over $CaCl_2$, 40 ml) for 19 h. The polymer was then filtered under vacuum over sintered glass funnel and washed with $CHCl_3$. The polymer was dried in a vacuum oven at 45°C for 24 h, to obtain the product as white beads (5.86 g, capacity = 0.925 mmol/g piperazine (by titration)) (1.14 mmol/g, from weight increase and elemental analysis).

Resin conditioning

Resins in the wet form were conditioned by cyclic exhaustion with 1 M HCl and regeneration with 1 M NaOH and finally washed thoroughly with a large volume of distilled water and stored in water. Resins had 1.95 and 0.91 mmol/g proton capacity for PS-PIP and MC-PIP, respectively (determined by resin titration).

Reagents and solutions

$NaCN$ solutions with pH maintained above 11 by using NaOH, to avoid HCN formation, were used to dissolve metal cyanide complexes. Stock solutions were prepared by dissolving $K_2Ni(CN)_4$, $KAu(CN)_2$, $K_4Fe(CN)_6$, $KAg(CN)_2$ and $CuCN$ (Johnson Matthey and Aldrich, A.R. grade) in $NaCN$ solution. Real cyanide leach liquors were obtained by leaching a gold mineral ore from Brazil at two different leaching pHs 9.8 and 11.0. The composition of these solutions is shown in Tab. 1.

Hydrochloric acid, sodium chloride and sodium hydroxide (Merck, AR) were used in the preparation of the different solutions for titration of the resin. Potassium bromide (Merck, for spectroscopy) was used for the preparation of the pressed disks for FTIR.

Tab. 1. Composition of the metal cyanide leach solutions.

Metal	Leaching pH 9.8	Leaching pH 11
Gold (Au)	30.7 ppm	38.1 ppm
Silver (Ag)	1.7 ppm	2.0 ppm
Copper (Cu)	2.4 ppm	2.0 ppm
Iron (Fe)	3.7 ppm	87.6 ppm

Proton exchange capacity determination

Piperazine resins were converted to the chloride form by treating with 1 M HCl solutions overnight. Finally they were washed thoroughly with a large volume of distilled water and dried between filter sheets and stored in wet condition. The PS-PIP resin has a practical proton exchange capacity of 1.95 mmol/g (dry) as compared to the total exchange capacity of 1.84 mmol/g (dry) N analysis. For MC-PIP and 0.91 mmol/g (dry) exchange capacity as compared to the total of 1.14 mmol/g (dry) by total N analysis.

Practical exchange capacity of both resins was determined by two different procedures. In the first procedure, 0.2 g of resin in the chloride form was equilibrated with an excess of a standard NaOH solution (0.1 M) overnight and later the excess of NaOH was titrated with a standard HCl solution (0.1 M). In the second procedure, titrations of 0.2 g of resins with a standard NaOH solution (0.1 M) were performed.

Resin titration

The acid-base properties of the resin were investigated by titrating the acid form of the resin with standard sodium hydroxide and hydrochloric acid solutions, respectively. A weighted amount (between 0.2–0.4 g) of the resin in the acid form was suspended in a known volume of the aqueous solution. The acidity ranged between pH values of 2 and 12. The lower limit was chosen so that the junction potential could be kept constant. The titrations were followed potentiometrically at 25 °C with an Orion Research model 701A digital Ionalyzer, equipped with a Ross type Orion Research 810100 pH electrode with a salt bridge of the same composition of the external solution (0.1 M NaCl), and with a porous glass junction to keep the resin outside the salt bridge. The cell was calibrated before each titration, during which the standard potential was determined by normal procedures.^[21]

Gold cyanide extraction procedures

Sorption experiments: For measurement of equilibrium sorption, small-scale dynamic contacts between resin and metal cyanide complexes were effected. Samples between 0.05–0.2 g of resins, 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 with a high-speed centrifuge, 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 absorption spectrophotometry (Perkin-Elmer 2380

AAS 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.

FTIR spectroscopic studies

FTIR spectra of piperazine and PS-PIP resin samples equilibrated with aqueous solutions of different pH (2, 8, 12 and 14) were recorded with a BOMEM MB120 Fourier Transform Infrared Spectrometer (4000–700 cm⁻¹) (32 interferograms were scanned at 2 cm⁻² resolution).

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 both for 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. The calibration standards were the appropriate metal foils (AR, Johnson & Matthey) etch cleaned in vacuum using an argon ion beam. Such calibration gives a certainty in binding energy of better than 0.05 eV, although most binding energies stated in this publication are quoted with errors of ±0.1 eV due to uncertainties arising from the subtraction of static charge shifts.

Samples of the resin in bead form were cooled to ca. 150 K (to minimize any thermal induced radiation damage) before excitation with Mg K_α X-rays operated at power of 300 W. The analyzer pass energy was maintained at 50 eV. As the resins are electrically non-conductive they acquire an equilibrium positive electrostatic charge under irradiation, necessitating the use of a binding energy reference point. The C(1s) photoelectron peak BE of the piperazine resin back-bone was adjusted to the C(1s) BE value for polyethylene of 284.8 eV.^[22] The bulk of its carbon content is in the form of (CH₂)_n backbones and aromatic rings pendant on the chain. For the purpose of analysis of the photoelectron spectroscopic data this resin can be viewed as consisting of carbon atoms in the general groupings of phenylene, methyl, methylene and methyldene (assigned on the basis of non-hydrogen valence). Although the use of polyethylene for the BE reference point applies strictly only for the methylene carbons, any aliphatic carbon not-attached to a highly electronegative or electropositive group will in general have the same BE within experimental error. Interestingly, in simple aromatic systems the same holds true as benzene carbons have reported C(1s) BE values of 284.8^[23] to 284.9^[24] eV. However, ring substituents can have a major effect: e.g. in methylbenzene, whilst the methyl C(1s) is 284.7 eV, the average ring C(1s) value is 285.2 eV. For the piperazine resin about half the carbon content is phenylene. Using the weighted means of all C(1s) binding energies the peak maxima assigned was 284.6 eV. The possibility of radiation damage was monitored by comparing the Au(4f) photoelectron peak shape at the beginning and end of the acquisition period. In no instance were there any significant differences in the binding energies or peak widths within acquired sig-

nal-to-noise (S/N) ratio. XPS data are plotted here as total counts in each 0.05 eV channel. Adequate S/N ratios were achieved by acquiring multiple scans over each region of interest. The number of scans was chosen according to the photoelectron cross section and expected elemental concentrations. Consequently, N(1s) regions were scanned 50 times each (a total of 5 s/channel) and Au(4f) regions 25 times (2.5 s/channel). Spectra were smoothed using 5 passes of a moving polynomial fit.

Results

1. Resins synthesis

We chose to study the reactions between monosubstituted piperazines and two classes of polymers, aromatic styrene-divinylbenzene copolymers (Amberlite XE-305) and aliphatic poly[(glycidyl methacrylate)-*co*-(ethylene dimethacrylate)]. This choice was based on the following reasons:

1. Both polymers are widely used in synthesizing chelating ion exchange resins. XE-305 was described in a series of publications from our laboratory and poly[(glycidyl methacrylate)-*co*-(ethylene dimethacrylate)], originating from the Institute of Macromolecular Science in Prague, Czechia, is easily available and widely used.^[25–29]
2. Both polymer series incorporate an electrophilic group, which can be readily used for reacting with the secondary amine nitrogen of the piperazine (Pi) ligand, yielding analogous polymers and modes of attachment.
3. The variance in the polymer structure allows comparison of various factors, important to the metal-binding reaction efficiency.

Fig. 1 shows the reaction between chloromethyl XE-305 and piperazine-ethanol; the reaction is expected to proceed mainly by substitution of the secondary amine and *not* by alkylation of the tertiary amine. This is corroborated by the behavior of the analogous reaction in solution between benzyl chloride and piperazine-ethanol. Yet a certain small percent of quaternization should be considered as possible. The product is designated as PS-PIP.

Fig. 2 shows the analogous reaction with MC-PIP, the (glycidyl methacrylate)-*co*-(ethylene dimethacrylate) copolymer. The reaction proceeds by ring opening of the epoxide group by the secondary amine nitrogen of the ligand Pi, and quaternization of the tertiary amine of Pi is even less likely. The product is designated as MC-PIP. Comparing the structures of both polymers, PS-PIP incorporates 1.84 mmol/g of Pi groups, whereas MC-PIP incorporates only 1.14 mmol/g of Pi groups. The practical hydrogen exchange capacity is 1.95 mmol/g (dry) for PS-PIP and 0.91 mmol/g (dry) for the MC-PIP resin. The fact that the practical hydrogen exchange capacity of the PS-

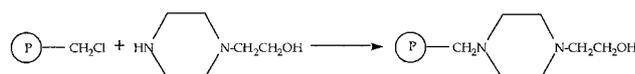


Fig. 1. Synthetic route of PS-PIP resin.

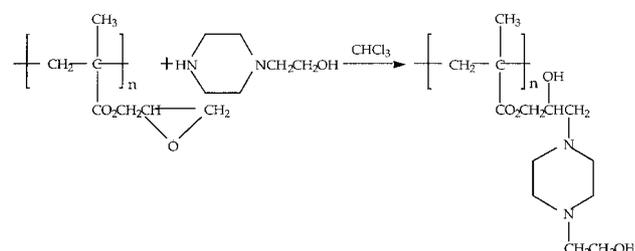
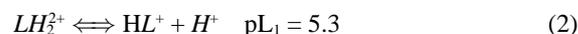
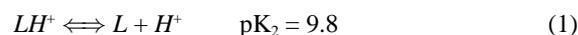


Fig. 2. Synthetic route of MC-PIP resin.

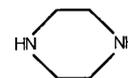
PIP resin is higher than the Pi group concentration could be explained by the fact that a partial protonation (around 5–10) of the second nitrogen of the piperazine group was observed on the titration curves.

2. Acid-base characterization

The necessity for protonating the amine groups of weak-base resins before interacting with gold cyanide prompted an investigation of acid-base properties of the ion exchanger. The basicity of a weak-base resin is determined by the pH value at which protonation of the functional group takes place. In turn this is influenced by factors such as the aqueous-phase basicity of the amine, and inductive and steric effects. Such factors may be introduced by the attachment of the functional group to the matrix of the resin. The ligand analogue of this resin, piperazine (L) has been characterized in terms of its acid-base properties in aqueous solutions according to the following protonation reactions^[18]



Where L:



Upon substitution of the amines, the two amine groups in the Pi ligand become non-equivalent in regard to their acid-base properties. Accordingly, there is a need to assign the two nitrogens as N_1 (the vicinal close to the backbone) and terminal (remote from backbone) as N_2 . The pK values of N_1 and N_2 are expected to shift due to two factors: (a) the immediate chemical environment, i.e., distance from the backbone, and polarity of an adjacent chemical group and (b) the overall ionic environment, i.e., the concentration of ionic groups inside the

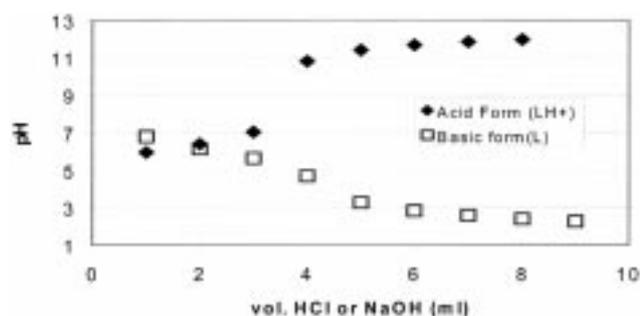


Fig. 3. Potentiometric titration curves of the acid (LH^+) and base (L) forms of the piperazine resin. Mass of resin 0.4 g and 0.1 M NaOH and HCl solutions were used respectively for resin titration.

resin; for example, changes in functional group concentration in the resin phase.

If, for the present, we ignore the variation in the overall ionic environment and consider only the immediate one, it is reasonable to expect that N_1 and N_2 in the MC-PIP resin will show similar properties, whereas in PS-PIP there are expected differences between them, as N_1 is exposed to a steric crowdedness effect and this may lead to N_2 being protonated first. In MC-PIP, both N_1 and N_2 are expected to have similar chances for protonation in the first step.

Simplified titration curves of the acid and base forms of the PS-PIP resin are shown in Fig. 3. Graphical analysis of both titration curves show an equivalence point corresponding to half of the total content or nitrogen capacity. Additionally, the close to neutral proton concentration values obtained for both forms (acid and base), \approx pH 5 for the acidic form and \approx pH 7 for the basic form, indicate that the acid-base properties of both nitrogen atoms of the piperazine functionality were strongly shifted. In both cases the titration curve shows just a single S-shape function indicating the neutralization of one of the N of the piperazine group. Then, as preliminary step this titration behavior could be explained assuming the following neutralization reactions:

a) When titrating the basic form with HCl



b) When titrating the acid form with NaOH



L being the terminal nitrogen atom of the functional group of the resin (N_2).

2.1 Acidity constant determination of piperazine group ($pK_{H(a)}$)

Accurate titration curves of the piperazine resins (PIP-PS and PIP-MC) were used for the determination of the

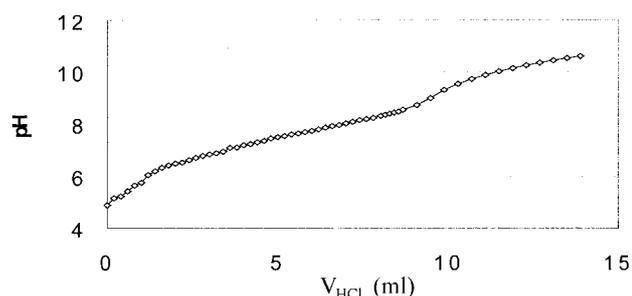


Fig. 4. Potentiometric titration data for the acid form of the piperazine resin in a 0.10 M solution of NaCl. Mass of resin 0.21 g and NaOH 0.05 M were used.

pK_a value of the attached piperazine group. An example of the titration of the acid form of PS-PIP is shown in Fig. 4. As can be seen, the addition of a small volume (less than 0.8 ml) of NaOH causes a sharp change of the pH indicating that just a small percent of the piperazine groups is in the form of LH_2^{2+} and mostly as HL^+ . The modified Henderson-Hasselbach^[30] equation was used as base for quantitative presentation of the potentiometric curves of the piperazine resins. By using this equation the acid-base properties of ion exchangers are characterized by a constant $pK_{H(a)}$ expressed in the linear equation

$$pH = pK_{H(a)} + n \log \frac{a}{1-a} \quad (5)$$

Where a is the degree of dissociation of the ion exchanger functional groups and the pK_H and n are empirical constants.^[30,31] If $n = 1$ then Eq. (5) is a logarithmic form of the formal dissociation constant of the ion exchanger functional group. The physical meaning of the constant $pK_{H(a)}$ is often named the dissociation constant index^[30,32,33] with addition of some restrictive definitions (as half neutralization degree, mean, etc.). Although a rigorous connection of this constant with physically understandable properties has not been established, it is used as a measure of the acidity of ion exchangers, implying that it has much in common with the dissociation constant. Numerical analysis of the pH versus the degree of dissociation of the acid (a) were used to determine the mean pK_H value 7.05 ± 0.12 (means of three titrations) at 298 K. An example of the $pH = 7$ a for the data of Fig. 4 are shown in Fig. 5. This $pK_{H(a)}$ value is 3 units lower than those of the corresponding amine groups of piperazine itself in an aqueous solution. Similar shifts between ligand and ligand-bound-resin were previously observed by Green and Potgeiter^[34] for imidazole and pyridine based resins. The structure of the ion exchange resin as a complex polymer network, the steric effects promoting the inaccessibility of the N atoms of the active group, could explain the acid-base property changes. It does not seem possible to achieve the protonation of the second N_2

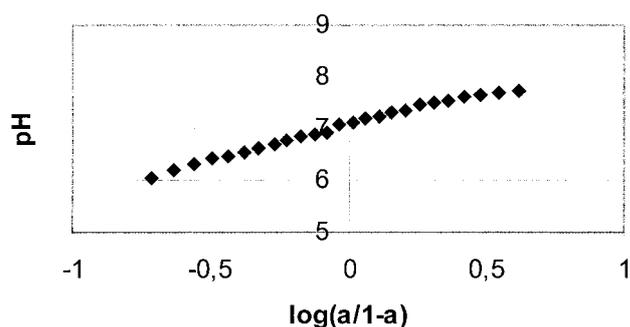


Fig. 5. Variation of pH as a function of $\log(a/1-a)$ (modified Henderson-Hassenbach equation) for curve of Fig. 4. Linear analysis of this function gives a $pK_{H(a)} = 7.01 \pm 0.12$ and $n = 1.3$.

of the piperazine group, probably due to the steric hindrance of the group bound to the amine.

The pK_a value obtained for the tertiary of the piperazine group is similar to those obtained by similar cyclic amine-based reagents as was described by Green and co-workers.^[10, 11, 34, 35] The pK_a values of these different values as those of the ligand analog are listed in Tab. 2. For those resins apparent pK_a values were calculated by using the following equation:^[36]

$$pK_a = pH_{50}(Cl^-) - \log[Cl^-] + \log([X/2]) \quad (6)$$

The pH value at which a resin is half protonated under particular conditions of solution ($pH_{50}(Cl^-)$ in the presence of chloride) is a measure of the basicity.

The basicity of a weak-base ion exchange resin has a profound effect on its capacity for gold cyanide at a particular pH value. The basicity of a weak-base resin is determined by the pH value at which protonation of the functional group takes place. This is influenced by factors as: i) the aqueous-phase basicity of the amine and ii) inductive effects, which may be introduced by the attachment of the functional group of the resin. Properties that are influenced by these factors could be the pK_a , $pH_{50}(Cl)$, $pH_{50}(Au)$. Both $pH_{50}(Cl)$ and $pH_{50}(Au)$ are typically determined in applied studies and could be used as an estimation of the pK_a value of the weak-base ion exchange resins. Fig. 6 shows the linear dependence of pK_a values of resins collected in Tab. 2 on both $pH_{50}(Cl)$ and $pH_{50}(Au)$ and suggests that those parameters could be used as an indirect indication of the pK_a values of weak-base anion exchange resins.

A prima facia, most of the resins described in Tab. 2 are potentially useful in the extraction of gold from alkaline cyanide solutions. Of course, one needs to consider the practical side of the ease of synthesizing these resins and the ambiguity in the structure of the functional group, adding another restriction, namely, the need to extract at a predetermined pH controlled by the pH of the gold mine leach solution (around pH 10). A further restriction

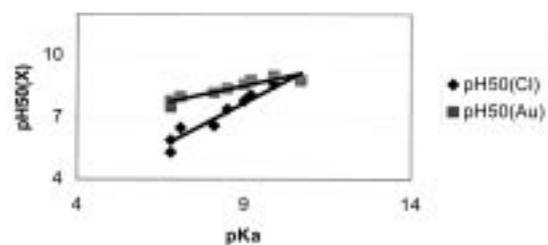


Fig. 6. Correlation of $pH_{50}(Cl)$ and $pH_{50}(Au)$ with the pK_a values of weak base ion exchange resins of Tab. 2.

is the selectivity in gold binding vis-a-vis other metal ions; and yet another restriction is the ability of the resin to be regenerated by the eluent and be available for reuse. These three restrictions eliminate most of the resins described in Tab. 2.

2.2 FTIR spectra analysis of PS-PIP piperazine resins at different pH values

Analysis of the IR spectra of the resin equilibrated to different pH values (2, 8, 12, 14) shows the absence of bands in the zone $2500-2200\text{ cm}^{-1}$, which can be assigned to the N—H stretching vibrations, asymmetric and symmetric, and the N—H deformation vibration of the protonated tertiary amine group for PS-PIP resin samples equilibrated at pH values 8, 12 and 14, where the resin should be in its base form according to the calculated $pK_{H(a)}$. Two strong bands in the region $2500-2200\text{ cm}^{-1}$ were observed for the sample equilibrated at pH 2, where the resin is in its acid form (protonated tertiary amine). Differences in the IR spectra of resin samples at the extreme pH values of 2 and 14 are shown in Fig. 7. These bands were compared with those broad bands obtained for the piperazine hydrochloride at 2200 and 2500 cm^{-1} and no appreciable change in the frequencies at which these peaks appear is observed,

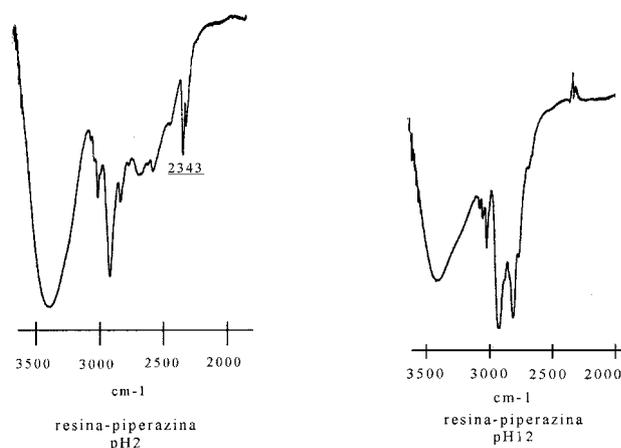


Fig. 7. FTIR spectra of the piperazine resins equilibrated at different pH values (a) pH = 2; (b) pH = 12.

Tab. 2. Structures and properties of weak base ion exchange resins.

Designation	Resin structure	Apparent $pK_a^{a)}$	A $pH_{50}(Cl)^{b)}$	B $pH_{50}(Au)^{c)}$	Functional group		Ref.
					mmol/g Weak-Base	mmol/g Strong-Base	
NH2		6.8	5.9	7.5	3.75	NA ^{d)}	[12]
NME2		8.1	6.6	8.2	5.92	0	[12]
NET2		6.8	5.3	7.8	2.82	0.08	[12]
STIM		9.0	7.8	8.6	4.02	NA	[12]
NHM		9.9 (ca.)	8.8 (ca.)	10.4 (ca.)	2.60	NA	[12]
GUANIDINE		n.d. ¹⁾	n.d.	n.d.	0.57 ^{e)} (ca.)	n.d.	[12]
DUIM		10.7	8.8	8.8	9.65	NA	[12]
DUMEIM		9.9	8.7	9.0	2.08	0	[12]
DUETIM		9.2	8.1	8.8	2.80	0	[12]
ALSTIM		8.5	7.4	8.3	0.26	NA	[12]
PDAA		10.2–10.7 8.5–9	8.5	10	–	–	[13] [15]
Duolite A7		≈5.8	–	–	–	–	[10]
Piperazine Resin PS-PIP		7.05	6.0	8.0	2.02	0.20	this work

^{a)} Apparent $pK_a = pH_{50}(Cl) - \log [Cl^-] + \log ([X_R]/2)$.

^{b)} $pH_{50}(Cl)$ denotes pH value at which a resin is half protonated under particular conditions of solution in the presence of chloride (Cl^-).

^{c)} $pH_{50}(Au)$ denotes pH value at which a resin is half protonated under particular conditions of solution in the presence of aurocyanide anion ($Au(CN)_2^-$).

^{d)} NA – Not applicable; n.d. – not determined, the high basicity of the resin makes determination impossible.

^{e)} The high basicity of the resin impedes the determination.

thus providing evidence that no specific interaction exists between chloride ions and the amine.

2.3 XPS analysis of piperazine resins at different pH values

An alternative spectroscopic technique for evaluating absorption states is X-ray photoelectron spectroscopy (XPS). This has proven particularly useful for determining the mechanism of adsorption of aurocyanide onto activated carbon and ion exchange resins^[14, 15, 37, 38] because of the capacity of the XPS method to establish chemical states from binding energy shifts and stoichiometries from peak intensities. XPS is used as complementary techniques to evaluate acid-base properties of ion exchange resins.

Marked chemical sensitivity was shown by the weak-base piperazine resin N(1s) photoelectron peak towards the extent of protonation. The effects of simple alterations in the environment of the amine were examined by equilibrating the resin in solutions of different pH values (2, 8, 12, and 14). The effect of pH on the piperazine amine N(1s) photoelectron peak is shown in Fig. 8 with single peak at basic pH values (8, 12, and 14) at 399.7 eV, while a broad doublet at pH = 2 with a shift of the N(1s) peak to higher binding energy (401.3 eV) has been observed. The presence of this doublet with two maxima at 399.7 and 401.3 indicates that both nitrogens (N1, N2) of the piperazine groups are not completely protonated and N2 remains unprotonated even at these low pH values.

These results are in agreement with the titration curves of the acidic form where the protonation of the second amine was not achieved completely. The N(1s) of the free N of the piperazine is totally formed at pH values higher than 8 and a small peak at high N(1s) energy values (402.3 eV) of the quaternary ammonium groups of the resin has been detected. The N(1s) BE shifts by ± 1.6 eV when protonated and this behavior would also be expected when other electrophilic species are attached to the amine nitrogen.

Hence, three different N types were detected, the tertiary N of the piperazine group (399.7 eV), the protonated form of the tertiary N (401.3 eV) and finally the N of the quaternary ammonium groups (402.3 eV). Deconvolution of the three peaks was performed and areas associated with each peak were also calculated and are shown in Fig. 9. It was difficult to determine with any accuracy the peak areas of very small peaks, i.e., the peak of the quaternary ammonium nitrogen in the sample at pH = 2 at 402.3 eV is very close to the protonated amine at 401.3 eV. The same holds for the protonated nitrogen of the piperazine group at pH = 8 where it was expected to have 5–10% protonated groups ($\text{pH} = \text{p}K_a + 1$). Consequently, in samples where the peak deconvolution procedure detected peaks with less than 5% of the total area (e.g.

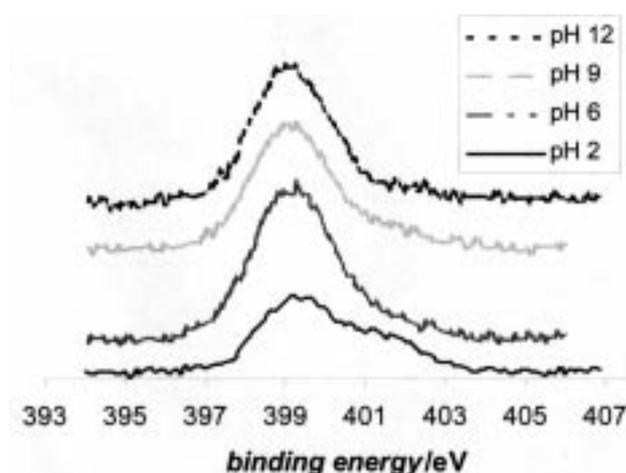


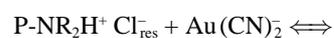
Fig. 8. The effect of pH on the piperazine amine N(1s) photoelectron peak. Protonation of the amine produces a shift to higher binding energy.

peak of the quaternary nitrogen at pH = 2, or the protonated nitrogen in sample at pH = 8) they were excluded in the deconvolution process due to the high error associated in their estimation.

3. Gold cyanide extraction properties

Dynamic equilibrium studies: The equilibrium extraction of $\text{Au}(\text{CN})_2^-$ from cyanide solution with both PS-PIP and MC-PIP resins was measured at different pH levels of a representative leaching solution containing 10 ppm of gold. The pH adjustment in the range 2 to 14 was made with HCl and NaOH. From the results plotted in Fig. 9, a quasi S-shaped function is observed with the extraction percentage falling rapidly from quantitative extraction at acidic pH values lower than 6 to low extraction values for pH above 10. The extraction of *all* the 10 ppm is quantitative at pH 6.0, but falls to 50% at pH 8.0. The resin loading capacity, in relation to the pH of the solution, was also determined (see Fig. 10, PS-PIP resin), and as can be seen, the gold loading capacity varies from 0.8 mmol/g (150 mg Au/g) at acidic pH value to 0.20 mmol/g (40 mg Au/g) with increasing pH from 2 to 10. This behavior may be attributed to the fact that the resin, as determined earlier, contains two different types of N functionalities. Taking into account the $\text{p}K_{\text{H(a)}}$ value around 7.05, the following reactions may be proposed to describe the gold cyanide extraction process:

1) at $\text{pH} < 7.05$ ($\text{p}K_{\text{H(a)}}$) the secondary amine group will be protonated as P-RNHR_2^+ and then the general mechanism of protonation and adsorption is based on the following steps:



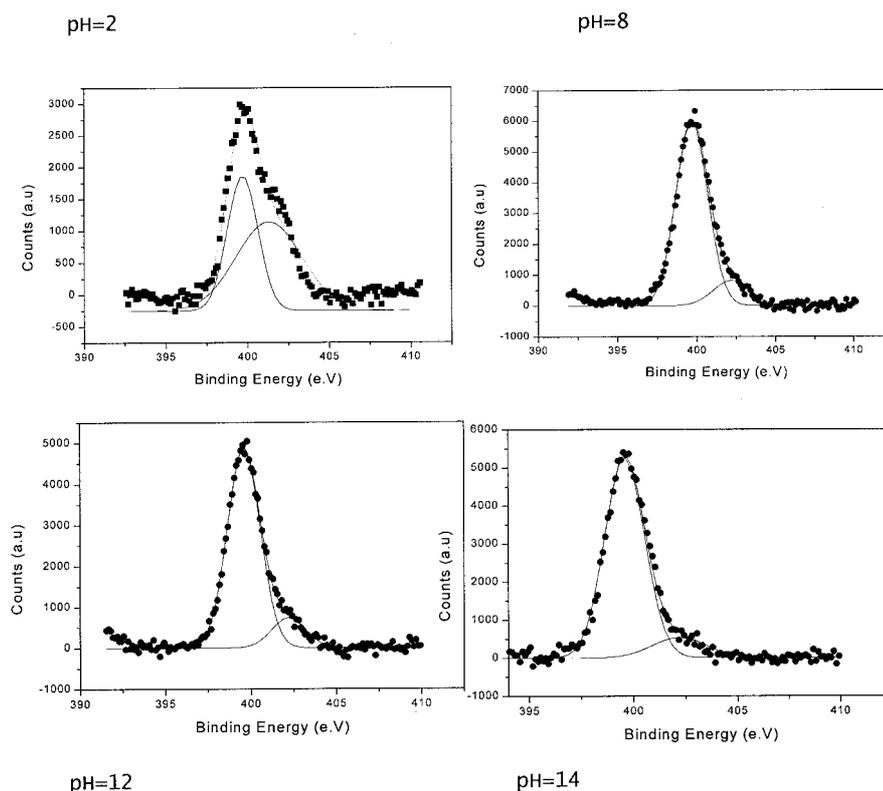
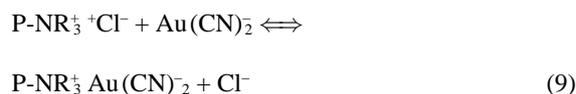


Fig. 9. Deconvolution of N(1s) peaks of piperazine resins at pH 2, 8, 12 and 14.

2) at $\text{pH} > 7.05$ ($\text{p}K_{\text{H(a)}}$) the tertiary amine group will be in the free base form as P-NR_2 and then the extraction reaction should involve a ligand substitution reaction of the CN^- of the gold cyanide complex by the amine group. Then, the gold cyanide extraction step could be described as follow:



Additionally it could be postulated that anion exchange reactions take place due to the existence of residual quaternary ammonium groups formed in the synthesis of the resin:



4. Elution studies

The loaded resin phases obtained in the extraction experiments were used for the study of the elution of $\text{Au}(\text{CN})_2^-$. Taking into account different possible extraction mechanisms, different types of elution solutions were used: aqueous solutions of NaOH, NaCN and thiourea/ H_2SO_4 and

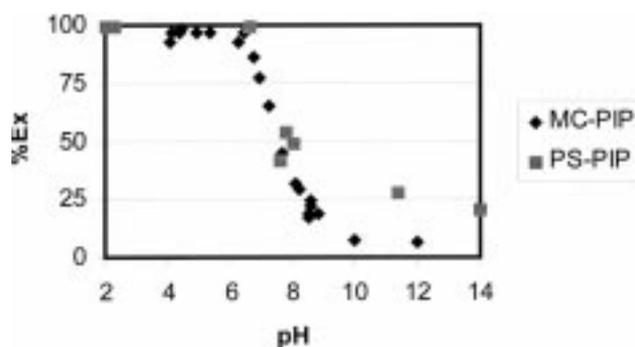


Fig. 10. Gold cyanide extraction percentage as a function of pH in the aqueous phase for PS-PIP resin (1.84 mmol Pi/g) and MC-PIP resins (0.95 mmol/g). Phase ratio was 0.2 g resin/20 ml of solution, $[\text{Au(I)}] = 10 \text{ mg/L}$.

ethanol/water solutions of NaOH. The elution data given in Tab. 3 and 4 point out that aqueous solutions of NaOH and NaCN gave partial recoveries (50–60%) while thiourea and ethanolic solutions of NaOH achieved quantitative recoveries of $\text{Au}(\text{CN})_2^-$ from the resin phase. This behavior may be understood taking into account the different gold extraction mechanisms involved vis-à-vis the nature of the eluents. In the case of aqueous solutions of NaOH and NaCN the deprotonation of the tertiary amine group occurs, causing release of the metal ions. In the case of thiourea possessing strong complexing properties

Tab. 3. Stripping of $\text{Au}(\text{CN})_2^-$ from loaded PS-PIP and MC-PIP resin.

Eluent	% stripping (PS-PIP)	% stripping (MC-PIP)
NaOH 1 M	60 ± 4	–
NaOH 1 M (v/v ethanol/water)	99 ± 3	93 ± 2
NaCN 5 gL ⁻¹	50 ± 3	45 ± 2
Thiourea 1 gL ⁻¹ /H ₂ SO ₄ 0.5 M	97 ± 5	98 ± 3 (UPC) 100 ± 5 (WIS)

Tab. 4. Complexation of Au by MC-PIP-cyclic experiments set 1 (piperazine-to gold 17.8).^{a)}

# NK	Cycle	Absorption		pH		initial conc. [Au] ₀ ppm
		%	%	initial	final ^{b)}	
NK-920	1	81.0	82.0	10.26	10.00	100
NK-922	2	97.0	70.0	8.50	4.37	100
NK-923	3	97.0	87.0	8.50	4.95	100
NK-924	4	96.5	87.6	8.50	6.42	100
NK-925	5	96.5	86.0	8.50	4.16	100
NK-926	6	93.0	91.0	8.50	4.05	100

^{a)} Conditions: 0.200 g MC-PIP (0.226 mmol piperazine); cycling conditions; 1. Absorption: 25 ml Au solution, 100 ppm Au (0.0127 mmol), 360 mg/l NaCN (0.18 mmol); 2. Elution: 25 ml 1 g/l thiourea in 1 M H₂SO₄ for 3–4 h, piperazine (on polymer): Au = 17.8 (mol ratio).

^{b)} After absorption.

towards Au(I) and Ag(I) metal ions, the metals are displaced directly and elution is effective. In the case of a NaOH aqueous/ethanol solution quantitative elution of gold cyanide from the resin was achieved as can be seen in Tab. 3. Experience with gold cyanide desorption from activated carbon^[34] shows that one factor that enhances the rate of elution is the effect of polar solvents such as acetonitrile, acetone, methanol and ethanol. This effect is attributed to an increase in the activity of the cyanide ion and a decrease in the activity of the aurocyanide ion in polar solvents as compared with water, and results in significant enhancement of the rate of elution.

5. Cyclic complexation and elution experiments

The extraction of gold cyanide from an initial solution of 10 mg/L (see Fig. 10) revealed the potential of the PS-PIP resin to bind quantitatively gold from real gold leach solution. Yet, it was necessary to ascertain that the resin would work effectively under cyclic complexation and elution conditions. The first experiment carried out (Tab. 4) was extraction from 100 mg/L of Au, followed by a rinse with water and elution with 1 g/L thiourea (Tu) in 1 M H₂SO₄. A 17.8 molar ratio of piperazine groups/gold was used. The extraction efficiency was close to 100% (93–97% complexation), while the calculated elu-

Tab. 5. Complexation of Au by MC-PIP cyclic experiments set 2 (piperazine-to gold 2.05).^{a)}

# NK	Cycle	Absorption		pH		initial conc. [Au] ₀ ppm
		%	%	initial	final ^{b)}	
NK-928	1	24	107.0	8.62	8.59	435
NK-929	2	22	96.5	8.62	8.60	435
NK-930	3	10.5	110.0	8.62	8.58	435
NK-931	4	18.4	91.0	8.62	8.51	435
NK-932	5	17	97.0	8.62	8.53	435
NK-933	6	7.4	115.0	10.08	10.00	435
NK-934	7	6.5	85.0	12.00	11.99	435

^{a)} Conditions: 0.100 g MC-PIP (0.113 mmol piperazine); cycling conditions: 1. Absorption: 25 ml Au solution 435 ppm Au (0.0552 mmol), 772 mg/l NaCN (0.18 mmol); 2. Elution: 25 ml 1 g/l thiourea in 1 M H₂SO₄ for 3–4 h; 3. Rinse; H₂O, NaHCO₃, H₂O, piperazine (on polymer): Au = 2.05 (mol ratio).

^{b)} After absorption.

tion efficiency was close to 90% (87–91%). The quantity of gold absorbed was 12.3 μmol (61.5 μg/g resin). A drop in the pH was noted: from 8.5 initially to ≈4.5, indicating that the eluent solution causes a large proportion of piperazine-resin groups to be protonated.

In the next cyclic experiment (Tab. 5), the conditions were altered: 2.05 molar ratio (Au/piperazine) and a higher Au concentration (435 mg/L). The result was that a steady pH was maintained. The percent absorption of the gold was ≈20% (17–24%) but this matched the available piperazine capacity (112 · 10⁻⁶ M Au/g vs. 113 · 10⁻⁶ M piperazine groups). It is worth to note also that a neutralization step was added after the acidic thiourea solution step.

6. Extraction from Brazilian mine solutions: Efficiency and selectivity

The extraction selectivity of PS-PIP resin on $\text{Au}(\text{CN})_2^-$ and other metal cyanides complexes in Brazilian mining leach solutions under different experimental conditions was evaluated. Fig. 11 and 12 present the loading of a number of cyano complexes $\text{Au}(\text{CN})_2^-$, $\text{Ag}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Fe}(\text{CN})_6^{3-}$ for two different leaching solutions (pH 9.8 and 11) obtained in leaching steps of the Brazilian mineral. The resin loading capacity for gold reaches 16 mg/g for pH 11 and 20 mg/g for pH 9.8. Under these conditions (at room temperature) substantial selectivity of gold is observed. From these values the distribution values of the different cyano complexes were calculated and from those the selectivity factors were calculated (Tab. 6). The selectivity order may be arranged as follow: $\text{Au}(\text{CN})_2^- \gg \text{Ag}(\text{CN})_2^- > \text{Cu}(\text{CN})_3^{2-} > \text{Fe}(\text{CN})_6^{3-}$.

Besides the ability to extract gold at the mine operating pH, the selectivity of the resin for the gold cyanide com-

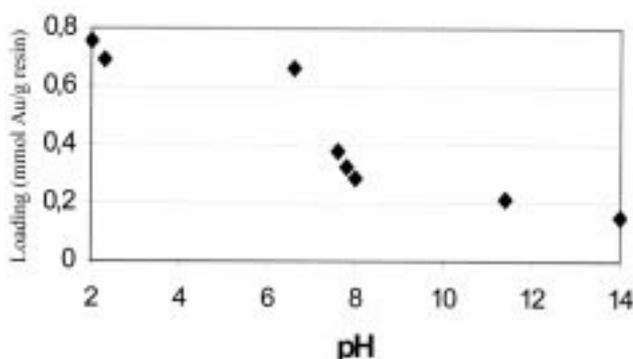


Fig. 11. Gold cyanide loading (mmol Au/g resin) as a function of gold cyanide concentration in the aqueous phase for PS-PIP resin (1.84 mmol Pi/g). Phase ratio was 0.2 g resin/20 ml of solution.

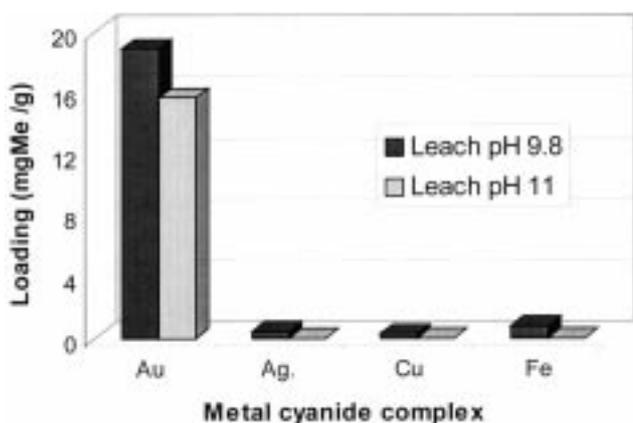


Fig. 12. Loading for the different metal cyanide complexes for PS-PIP resin (1.84 mmol Pi/g) – in two mining leach solutions: a) pH 9.8 and b) pH = 11.0. Phase ratio was 0.02 g resin/20 ml solution.

Tab. 6. Selectivity coefficients (S) of PS-PIP resin on metal cyanide extraction from gold mineral leaching solutions.

	Au(I)	Ag(I)	Cu(I)	Fe(II)
Y (mg M/g resin)	26.4	0.5	0.8	0.3
X (mg M/L solution)	11.7	1.2	1.6	3.4
$K_{S(Au)}$		5.5	4.6	26.5

plex must be high. Competition experiments on this resin were conducted using 1 to 50 ppm, depending of the metal cyanide, in basic cyanide solutions of 100 ppm. The selectivity of the resin is very high for gold.

Conclusions

The functionalization of a macroporous PS-PIP polymeric support with a piperazine group shows a substantial difference in behavior in terms of basic properties when

compared with the same functional group as ligand in solution. The basic properties of this ligand were decreased and diminished in terms of strength and acid capacity. Acid-base titrations have shown that:

- even in high acidic solutions it is not possible to protonate both nitrogens of the piperazine group;
- the piperazine group bound to a polymer shows a decrease in its basicity, from pK_a value of 9.5 for piperazine in aqueous solution to 7.05 when functionalized onto the polymeric matrix (PS-PIP).

Protonation of the N groups was studied by XPS analysis following the energy changes of the N(1s) after deconvolution of the XPS peaks. Three different types of N states were detected on the resin characterized by three different energy values: N(1s) of the free tertiary N of the piperazine at 399.7 eV, the N(1s) of the protonated N of the piperazine group at 401.3 eV and finally the N(1s) of quaternary ammonium groups produced during the functionalization of the piperazine resin also at 402.3 eV. Both N(1s) of the protonated form and the quaternary groups have a close peak at approximately 401.3 and 402.3, respectively. The assignment of the 402.3 eV to the bond to the quaternary amine group is based on measurements of samples of the resin equilibrated in highly basic solutions ([NaOH] 1 M) where the presence of protonated N of the piperazine group is eliminated. Additionally, the presence of free tertiary amine groups of the resin and protonated tertiary amine groups in samples of the resin equilibrated in acidic solutions of 0.01 M HCl was also demonstrated. These results are in agreement with the fact that the N_1 amine of the piperazine group (close to the polymer backbone) is not protonated.

Gold cyanide extraction properties show a typical S-shape function congruent with an ion exchange mechanism of a weak-base resin, with a decrease in the extraction due to the deprotonation of the N of the tertiary group at pH values between 6 and 8. A distinctive behavior was observed at higher pH values (pH range 9 to 14) where the extraction properties of the PS-PIP resin show a constant extraction trend independently of the pH of the aqueous phase – contrary to the expected – due to the completed deprotonation of the weak base.

PS-PIP and MC-PIP resins with a weak base functionality (tertiary amine group) show promising results when applied to the extraction of gold cyanide from cyanide media in terms of loading capacities achieving high gold loading of 150 mg/g PS-PIP resin at low pH values (lower than 6). At basic pH values close to normal conditions of resin in leach or resin in pulp operations (60 mg/g at pH values between 8 and 10) the PS-PIP and MC-PIP resins showed medium loading capacities.

Stripping of the gold cyanide complex from the resin was achieved efficiently by ethanolic sodium hydroxide solutions, while partial recovery was achieved with aqueous sodium cyanide solutions.

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