



The application of activated carbon for the adsorption and elution of platinum group metals from dilute cyanide leach solutions

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Synopsis

The research presented in this paper investigated the practical aspects of the recovery of platinum group metals (PGMs) from a dilute cyanide leach solution containing base metals, in a manner similar to that used for gold extraction in a typical CIP process, and focuses on both the adsorption and elution stages. The carrier-phase extraction of precious metals using activated carbon offers significant advantages over other processes in terms of simplicity, the high pre-concentration factor, rapid phase separation, and relatively low capital and operating costs. As a sorbent, activated carbon is still by far the most important material because of its large surface area, high adsorption capacity, porous structure, negligible environmental toxicity, low cost, and high purity standards.

Adsorption tests were conducted on a pregnant alkaline leach solution (0.15 ppm Pt, 0.38 ppm Pd, 0.1 ppm Au) resulting from cyanide extraction performed in column leach tests. The initial adsorption rates of Pt, Pd, and Au were very fast and recoveries of these three metals were approximately 90 per cent after 2 hours, and 100 per cent for Pt, 97.4 per cent for Pd, and 99.9 per cent for Au after 72 hours. The parameters that influence the extraction of PGMs and Au were examined to assess their relative importance during the adsorption process in order to provide the basis for process optimization. The concentration of thiocyanate was not identified as significant factor for PGMs adsorption, while Ni concentration was the most significant extraction process parameter. Base metal cyanide complexes adsorb and compete with the PGM complexes for sites on activated carbon, and while copper adsorption can be minimized by adjusting the residence time, Ni adsorbs at approximately the same rate as the PGMs, influencing the loading capacity and adsorption kinetics of the PGMs.

The feasibility of eluting platinum and palladium cyanide complexes from activated carbon using an analogue of the AARL process was investigated. Platinum and palladium elute from activated carbon almost to completion in 4 to 5 bed volumes at 80°C, while the elution of gold at this temperature is slow, with a significant amount of gold still to be eluted after 16 bed volumes. The equilibrium loading of gold is exothermic in nature (Fleming and Nicol, 1984) which will result in an increase in gold elution kinetics with an increase in temperature at similar pre-treatment conditions. A similar result was found for the elution of Pt and Pd. Cyanide pre-treatment was found to have a significant influence on PGM elution. Higher cyanide concentration in the pre-treatment step results in more efficient elution up to a point, and results suggest the possibility of an optimum cyanide concentration, beyond which elution efficiency starts decreasing due to increased ionic strength.

Keywords

activated carbon, adsorption, elution, platinum group metals, cyanide.

Introduction

The carbon-in-pulp or carbon-in-leach (CIP and CIL) processes have been the main commercial processes on almost every gold plant built since 1980 (Fleming, 1992; Van Deventer, 1984) with a stable interest in the process still existing (Vorob'ev-Desyatovskii *et al.*, 2012). The major advantages of CIP plants are that they require lower capital and operating costs, are mechanically robust, handle plant upsets remarkably well, and are highly tolerant to changes in feed composition (Fleming *et al.*, 2011). Since their establishment, considerable progress has been made in understanding the mechanisms and kinetics of gold adsorption onto activated carbon (Van Deventer, 1994), with research in the field still continuing (Vorob'ev-Desyatovskii *et al.*, 2012).

Alternative processing options that are less energy-intensive and are more able to deal with complex, lower grade ores are in demand, and according to Liddell and Adams (2012) there are potentially considerable technical and economic advantages to a robust hydrometallurgical processing route for PGM concentrates. Leaching of PGMs with cyanide has been proposed a number of times as a promising PGM process option. Mwase *et al.* (2011) proposed a conceptual flow sheet for heap leaching of PGMs from a low-grade ore concentrate. Chen and Huang (2006) and Huang *et al.* (2006) investigated two-stage selective pressure-leaching cementation from low-grade Pt-Pd sulphide concentrates. Shams *et al.* (2004) leached spent catalyst with cyanide and claimed that among the vast variety of methods available, the cyanide

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leaching method is more cost-effective and environmentally friendly than conventional smelting and acid-recovery techniques. Platinum Australia Limited (PLA) in conjunction with Lonmin plc (Lewins, 2003) developed the Panton Process, in which low-grade flotation concentrates are subjected to low-temperature calcination followed by cyanide leaching at elevated temperature to dissolve the PGMs, Au, and base metals. These are then recovered from solution by precipitation (Bax, 2004) to produce a high-grade PGM and base metal concentrate suitable as direct feed to a refinery. On Panton project ores, the process gave significantly higher recoveries and much higher final product grades than standard metallurgical processes for PGMs. McInnes *et al.* (1994) and Bruckard *et al.* (1992) studied the ambient and elevated temperature cyanidation of ore from the Coronation Hill deposit in Australia. Although the leaching step has been investigated, research regarding the upgrading and recovery of the PGM cyanide liquor with activated carbon has hitherto received little attention.

Aguilar *et al.* (1997) studied the adsorption kinetics of precious metal cyano complexes onto activated carbon through their newly-developed capillary electrophoresis (CE) method, and found that Pt and Pd cyanides were selectively adsorbed onto carbon in a short time (100 per cent), while Rh cyanides showed much lower adsorption (40 per cent). Roijals *et al.* (1996) also found that Pt adsorbs fairly quickly onto activated carbon, and in addition, studied the PGM adsorption potential of several impregnated and ion-exchange resins. Desmond *et al.* (1991) evaluated the loading of activated carbon with PGMs and found that more than 99 per cent of the Pt and Pd, but less than 15 per cent of Rh, were removed from solution after contacting samples of leach solution with activated carbon for 1 hour in stirred beakers using ten times the recommended amount of carbon

Although some literature regarding the feasibility of PGM adsorption exists, fundamental research regarding the elution process of PGMs, the mechanism of adsorption and elution, or the reason for poor Rh adsorption onto activated carbon is lacking. Milbourne *et al.* (2003), in an evaluation of the use of hydrometallurgy for the direct processing of PGM concentrates, stated that for the well-proven gold recovery process, the carbon is readily strippable and can be recycled many times. PGMs, however, may not be as easily recovered in a stripping process, as evidence suggest that PGMs adsorbed on carbon from a chloride solution matrix reduce to the metallic state.

In this paper we investigate the use of activated carbon as a precious metal recovery option from leach solutions resulting from the cyanidation of platinum-bearing ores or concentrates, in order that the flow sheet can be assessed for technical feasibility and economic viability. The two major steps of the process, i.e. the adsorption and elution sections, were investigated and the effects of operating variables on process performance were determined.

Adsorption

Experimental

A coconut-based granular activated carbon supplied by Marlyn chemicals (Pty) Ltd, South Africa, with a BET surface

area of 1200 m²/g and iodine number 1075 mg/g according to the specifications of the supplier, was used for the adsorption and elution experimentation work. Prior to use, the adsorbent was washed with hydrochloric acid (5 per cent) at 25°C and subsequently dried at 80°C for 48 hours. The water-washing was stopped when the pH value of the suspension remained constant at 7. This operation significantly reduces the amount of superficial mineral impurities and powder (ash).

The activated carbon was sieved to obtain a particle size fraction between 1180 and 3350 µm, with a *d*₅₀ grain size of about 2360 µm, for all the experiments.

The adsorption tests were carried out by contacting the carbon with 500 ml of the cyanided solution (as per Table I and II in the subsequent sections) and adjusted to an appropriately high pH to prevent the formation of HCN gas by adding NaOH (1N). Tests were performed with the traditional rolling bottle method in 2.5 litre bottles containing 500 ml of the solution at room temperature. In order to ensure that a pseudo-equilibrium was attained, the mixture was rotated for 72 hours, this duration being selected on the basis of gold adsorption experiments (assuming pseudo-equilibrium conditions) reported by Van Deventer (1984) who showed that equilibrium was still not achieved between gold cyanide and activated carbon after several weeks of adsorption. Liebenberg and Van Deventer (1997) indicated that pseudo-equilibrium isotherms could be used, but carbon/solution contacting times of less than 72 hours could lead to ineffective modelling.

Table I

Composition of pregnant leach solution from column test

| Constituent | Concentration (ppm) | Constituent | Concentration (ppm) |
|-------------|---------------------|-------------------------------|---------------------|
| Pt | 0.150 | Pb | 0.01 |
| Pd | 0.380 | Ca | 18.500 |
| Rh | 0.010 | Li | 0.007 |
| Ru | 0.010 | Na | 6137 |
| Ir | 0.001 | K | 23.15 |
| Au | 0.100 | Mg | 1.67 |
| Ag | 0.040 | NO ₃ | 0.000 |
| Cu | 18.840 | Cl ⁻ | 12.600 |
| Co | < 1 | CN ⁻ | 12.5 |
| Ni | 18.300 | SCN ⁻ | 3670 |
| Fe | 47.300 | S ²⁻ | 2.600 |
| Zn | 0.060 | SO ₄ ²⁻ | 11230 |

Table II

Individual levels of the seven operating factors

| Operating factor | (-) | (+) |
|---------------------------------|------|------|
| pH | 9.5 | 12 |
| [Cu(I)] (ppm) | 10 | 100 |
| [Ni(II)] (ppm) | 10 | 100 |
| [CN] (ppm) | 100 | 300 |
| [SCN] (ppm) | 50 | 100 |
| [PGMs] (ppm) {Pt, Pd, and Au} | 0.63 | 2.03 |
| Carbon concentration [AC] (g/l) | 10 | 20 |

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Solution sampling was done at pre-determined times (0, 1, 2, 3, 6, 24, 48, and 72 hours) and involved withdrawal of 5 ml of solution using a syringe filter (to remove any carbon fines that might be present in the solution) followed by ICP-MS analysis of the filtrate. The uptake of metals onto the activated carbon was determined from the difference of metal concentrations in the initial and final solutions. Due to the presence of copper, sulphide, and thiosulphate, the free cyanide (CN^- and HCN) was measured by potentiometric titration instead of the more traditional method of titration with silver nitrate using rhodanine as the indicator. Where necessary, SCN^- and S^{2-} were measured by high-performance liquid chromatography (HPLC) and ion chromatography techniques, respectively.

Apart from initial adsorption tests, all experiments were carried out with synthetic solutions that were made up by dissolving $\text{K}_2\text{Pt}(\text{CN})_4$, $\text{K}_2\text{Pd}(\text{CN})_4$, and $\text{KAu}(\text{CN})_2$ in distilled water. (Chemical composition displayed in Table II.)

Adsorption results

Initial adsorption tests were conducted on a pregnant alkaline leach solution resulting from cyanide extraction performed in column leach tests on ore following a base metals extraction. Table I details the components identified in the pregnant leach solution and their concentrations. The constituent concentrations in the solution were analysed using either ICP-MS or ion chromatography-HPLC techniques.

The adsorption profiles resulting from contacting the solution with activated carbon for both precious and base metals are shown in Figure 1. It is evident that the extractions of Pt and Pd are comparatively fast for the first 120 minutes, and then start to slow down, achieving close to 100 per cent adsorption for Pt, Pd, and Au.

Ni adsorption exhibits kinetics similar to those of Pt, Pd, and Au. The high initial uptake rate of Ni may also be ascribed to the availability of a large number of adsorption sites on the adsorbent surface. Marsden and House (2006) observed that despite the highly selectivity of activated carbon for gold and silver over most other metal species, high loadings of non-precious metals can be achieved onto activated carbon in the absence of significant precious metal values.

Figure 1 reveal that, after one hour, Cu adsorption was roughly 5 per cent while Pt extraction was between 95 and 100 per cent. Cu co-extraction might therefore be reduced by minimizing the residence time during adsorption. Copper adsorption increased considerably over time from 5 per cent after one hour to between 85 and 90 per cent after 72 hours. According to Boshoff (1994), Adams (1991), and Lu *et al.* (2002), copper adsorption depends on the copper cyanide complex present, which is determined by the solution conditions such as pH, temperature, and mole ratio of copper to cyanide. $[\text{Cu}(\text{CN})_2]^-$ adsorbs strongly and is favoured at low pH values and low cyanide concentrations, whereas $[\text{Cu}(\text{CN})_4]^{3-}$, which adsorbs very little, is formed at pH values above 10 and cyanide strengths above 200 ppm. $[\text{Cu}(\text{CN})_3]^{2-}$ is the most stable form of copper cyanide. Due to the relatively low amount of free cyanide present (12 ppm), it is expected that a mixture of $[\text{Cu}(\text{CN})_2]^-$ and $[\text{Cu}(\text{CN})_3]^{2-}$ was present.

No significant changes in the solution concentrations of Rh and Fe were observed after 72 hours. At such low solution concentrations, it is possible that Rh reaches equilibrium very rapidly at a concentration where analytical errors are significant. It is expected that Rh is present in the solution as an octahedral $\text{Rh}(\text{CN})_6^{3-}$ (Aquilar *et al.*, 1997), which is a strong cyanide complex with a stability constant of 47 (Read *et al.*, 1994), and therefore in comparison to the similar strong cyanide complexes of $[\text{Pt}(\text{CN})_4]^{2-}$ with a stability constant of 40 and $[\text{Pd}(\text{CN})_4]^{2-}$ at 51.7 (Monlien *et al.*, 2002), which does adsorb well, it is likely that the low adsorbance of Rh are due either to the high negative charge of $\text{Rh}(\text{CN})_6^{3-}$ or the shape and size of this molecule. In the case of Fe, the very low adsorption is supported by Vorob'ev-Desyatovskii *et al.* (2012), who showed that neither $\text{K}_3[\text{Fe}(\text{CN})_6]$ nor $\text{K}_4[\text{Fe}(\text{CN})_6]$ in neutral and alkaline (pH 10.5) aqueous solutions are adsorbed on an activated carbon (GoldcarbWSC207C-GR).

Two sets of laboratory-scale experiments were conducted using synthetic solutions prepared as previously described, whose chemical composition is displayed in Table II. The first set consisted of equilibrium tests that were designed to generate the optimum operating conditions of the adsorption process. The second set of experiments consisted of loading capacity studies.

From the literature (Das, 2010; Adams *et al.*, 1987; Lu *et al.*, 2002) it is known that the solution pH is one of the most important variables for the overall adsorption process. The effect of pH is shown in Figure 2 and indicates that a decrease in pH leads to an increase of the uptake of Pt and to a lesser extent Au ions by the adsorbent. Pd was found to be insensitive to the pH. This, together with the small effect on Au adsorption, may be ascribed to the fact that virgin activated carbon was used to perform the experiments and thus the high availability of sites on the activated carbon. As the activity of the activated carbon decreases (indication of the sites available for adsorption) the effect of pH is expected to become more pronounced. A lower pH appears to favour the adsorption of PGMs but is constrained by a safe working limit at approximately 9.5 due to the formation of HCN gas at lower cyanide solution pH values.

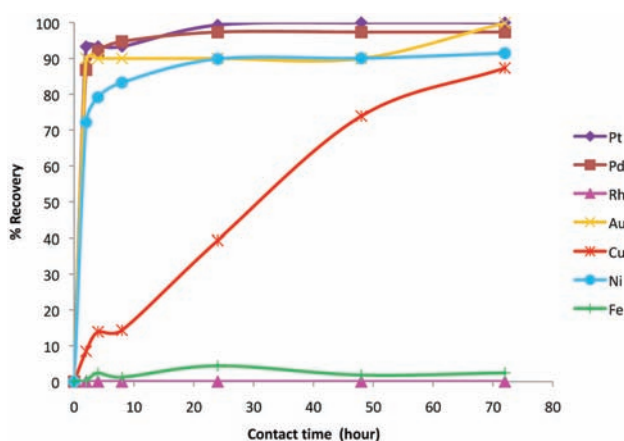


Figure 1—PGM and BM adsorption kinetics: pH = 10, CN = 12.5 ppm, activated carbon = 10 g/l, rotational rate = 105 r/min, contact time = 72 h, temperature = 25°C

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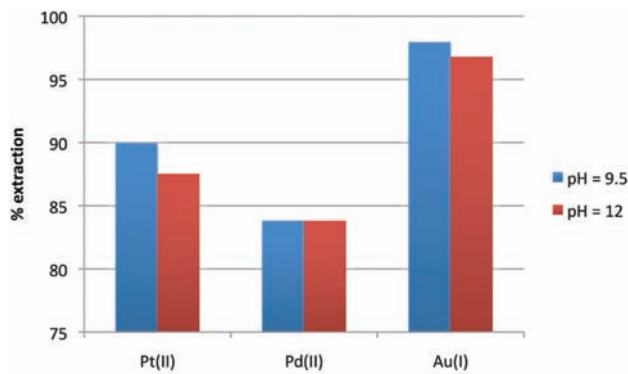


Figure 2—Effects of pH on the extraction efficiency of PGMs (Pt, Pd, and Au) (contact time: 2 hours; rotational rate: 105 r/min; adsorbent concentration: 15 g/l; temperature: 25°C; Cu: 55 ppm; Ni: 55 ppm; CN: 200 ppm; SCN: 75 ppm; PGMs: 1.33 ppm)

It was observed from the experimental data that the Cu concentration had significant effects on Pt and Pd extractions. The deleterious effect on Au adsorption was found to be less significant under these specific conditions. An increase in copper concentration caused a decrease in the Pt and Pd extraction as shown in Figure 3. Additional experimentation indicated that the rate of Pt adsorption is dramatically reduced in the presence of copper when loading from a higher initial solution concentration of 5 ppm Pt, while that of gold remains almost unchanged. It was concluded that the presence of copper (especially when in the $[\text{Cu}(\text{CN})_2]^-$ and $[\text{Cu}(\text{CN})_3]^{2-}$ forms and co-adsorbing) in the adsorption circuit will have a larger impact on the adsorption of platinum and palladium than on the adsorption of gold. The adsorption time and the amount of copper present in the circuit will therefore play a very important part, and need to be taken into consideration in the design of the PGM adsorption circuit to ensure sufficient PGM recovery.

Ni was found to have the same effect on the adsorption of PGMs as did copper, as indicated by Figure 4. The effect of Ni, however, was more pronounced, as the rate of Ni adsorption is similar to the rate of PGM adsorption, as indicated in Figure 1. While the loading of Cu can be reduced by decreasing the residence time (e.g. to less than 2 hours), the loading of Ni cannot. Ni adsorption, as opposed to Cu adsorption, also seems to be less influenced by the cyanide concentration. Fisher and LaBrooy (1997) found that the Ni adsorption remained unchanged as the cyanide concentration varied from 250 to 500 ppm. The effect of Ni on the adsorption of Au at these conditions was found to be insignificant (Figure 4).

Fleming and Nicol (1984) suggested that an increase in the concentration of free cyanide depresses the rate of loading and the equilibrium capacity of gold on activated carbons. This was also pointed out by McDougall *et al.* (1980) and is utilized in the elution of gold from activated carbons. The experimental results from this study, however, indicated that there is no change in the adsorption behaviour of the PGM system between 100 and 300 ppm CN^- for the first two hours of adsorption. The cyanide concentration is, however, expected to have a more significant effect on PGM adsorption under continuous loading conditions.

Davidson *et al.* (1979) stated that thiocyanate anions have a detrimental effect on the rates and capacity constants of gold adsorption when added individually to a synthetic solution at concentration levels of approximately 100 g/t, as found in the plant solution. However, in this work, experimental findings revealed that the presence of 100 ppm SCN^- did not appreciably affect the adsorption of PGMs. This observation is supported by the selective and quantitative extraction of Pt, Pd, and Au from the column leach liquor containing 3670 ppm SCN^- (Figure 1). Further investigations in this direction are warranted.

Initial metal concentration significantly affects adsorption. Higher initial adsorbate concentration provides a higher driving force to overcome mass transfer resistances of the metal ions from the aqueous to the solid phase, resulting in higher probability of collision between metal ions (PGMs) and the active sites (Rane *et al.*, 2010). Adsorption experiments showed a greater uptake of Pd and Au for the given amount of treated activated carbon at higher solution concentrations, while there was no effect on Pt extraction, as shown in Figure 5.

In order to determine the influence of a change in activity of the activated carbon on the adsorption of PGMs, a 10 g sample of activated carbon was contacted ten times with the same volume (1 l) of fresh synthetic BM – PGM liquor, and allowed to adsorb at room temperature for 2 hours under the

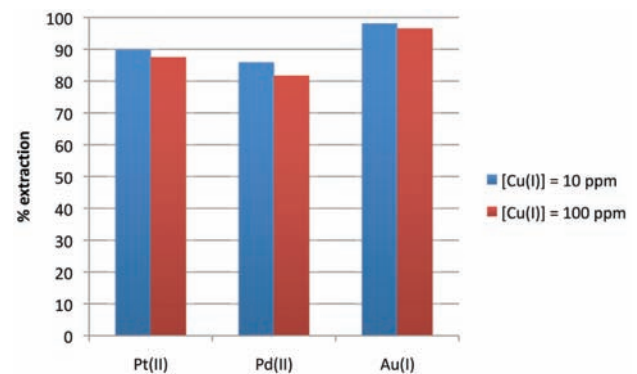


Figure 3—Effects of copper on the extraction efficiency of PGMs (Pt, Pd, and Au) (contact time: 2 hours; rotational rate: 105 r/min; adsorbent concentration: 15 g/l; temperature: 25°C; pH: 10.75; Ni: 55 ppm; CN: 200 ppm; SCN: 75 ppm; PGMs: 1.33 ppm)

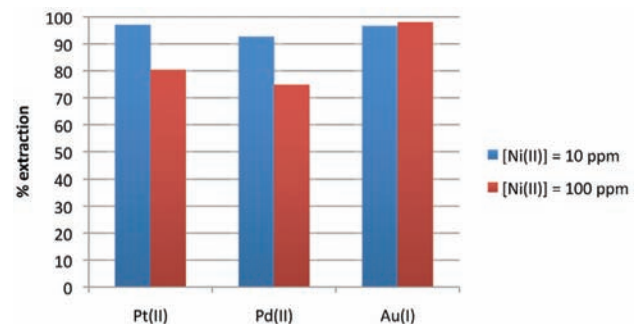


Figure 4—Effects of nickel on the extraction efficiency of PGMs (Pt, Pd, and Au) (contact time: 2 hours; rotational rate: 105 r/min; adsorbent concentration: 15 g/l; temperature: 25°C; pH: 10.75; Cu: 55 ppm; CN: 200 ppm; SCN: 75 ppm; PGMs: 1.33 ppm)

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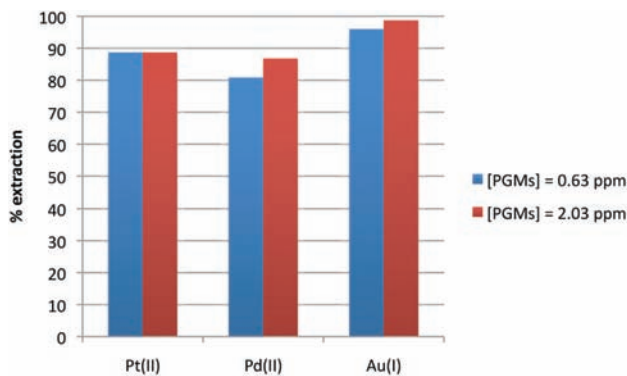


Figure 5—Effects of initial PGM ion concentration on their extraction efficiencies (contact time: 2 hours; rotational rate: 105 r/min; temperature: 25°C; pH: 10.75; Ni: 55 ppm; Cu: 55 ppm; CN: 200 ppm; SCN: 75 ppm; AC: 15 g/l)

optimum conditions as determined by the previous set of experiments (Figures 2 to 5). The activated carbon loadings were calculated from the cumulative changes in solution concentration before and after 2 hours of adsorption, and are shown in Figure 6 for Pt, Pd, and Au. For the first contact, recoveries from the fresh solution were 98 per cent for Pt and Pd and 100 per cent for Au within 2 hours, gradually decreasing to 39 per cent for Pd and 52 per cent for Pt, with the Au adsorption decreasing only to 98 per cent after 10 contacts (20 hours of contact time in total). Initial Ni adsorption was 89 per cent, and decreased to 13 per cent after 10 contact times. Even though the fractional extraction of Ni in each contact decreased fairly rapidly, the total quantity of Ni adsorbed was still substantial, due to the much higher Ni content in the feed solution. Due to the slower kinetics of Cu adsorption, as illustrated in Figure 1, the quantity of Cu adsorbed could be reduced substantially while maximizing PGM adsorption by allowing only 2 hours of adsorption time for each contact. The distribution of the metals on the activated carbon after 10 contact times can be seen in Figure 7. (Specific to relative concentrations at $t=0$ and distribution ratios as indicated.)

Elution

An analogue of the AARL process was used to investigate the feasibility of eluting platinum and palladium cyanide complexes from activated carbon. The AARL process involves the pre-treatment of the metal-loaded activated carbon with a relatively strong sodium cyanide and sodium hydroxide solution prior to elution with de-ionized water at high temperatures (90–130°C) and high pressure (200–300 kPa). An acid wash of the activated carbon with hydrochloric acid can be done either prior to the pre-treatment step or following the elution step, with the main purpose of removing calcium build-up from the activated carbon.

Experimental

Elution experiments were undertaken using the method described by Van Deventer *et al.* (1994). Activated carbon was loaded by means of the traditional rolling bottle method, using a synthetic solution containing an initial concentration

of 5 ppm each of Pt, Pd, and Au, for 65 hours, resulting in a PGM loading of approximately 650 g/t for Pt, Pd, and Au each. Typical industrial loadings of Au onto activated carbon before elution ranges from 2800 to 7000 g/t. Boshoff, (1994) suggested that the elution efficiency is independent of the amount of gold present on the activated carbon, and it was therefore deemed appropriate to select a low but convenient and easily detectable loading for this proof-of-concept study. Equal amounts of gold, platinum, and palladium were chosen in order to allow comparison between gold, the elution of which is well understood, and platinum and palladium, the elution of which is unknown.

Elution experiments were conducted with the loaded carbon in a glass column with a temperature-controlled water jacket. The aim of this study was to investigate the possibility of elution of Pt and Pd, and not to obtain the highest possible elution efficiencies. Therefore, a convenient temperature of 80°C was selected for the elution runs. The downward flow of eluant (2–4 bed volumes per hour at the elution temperature) through the column was controlled. A bed volume (BV) is defined here as the empty volume of the reactor (15 m³) that is occupied by the packed bed of carbon.

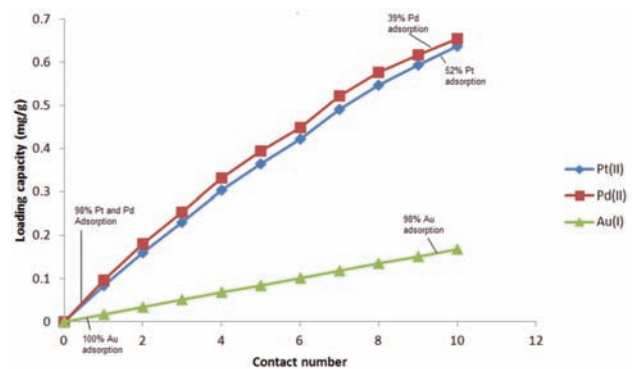


Figure 6—Consecutive loading of Pt, Pd, and Au onto activated carbon from a fresh synthetic BM-PGM solution at 2-hour intervals (adsorbent concentration: 10 g/l; temperature: 25°C; Cu: 10 ppm; Ni: 10 ppm; pH: 9.5; CN: 132 ppm; SCN: 100 ppm; PGMs: 2.03 ppm; rotational rate: 105 r/min)

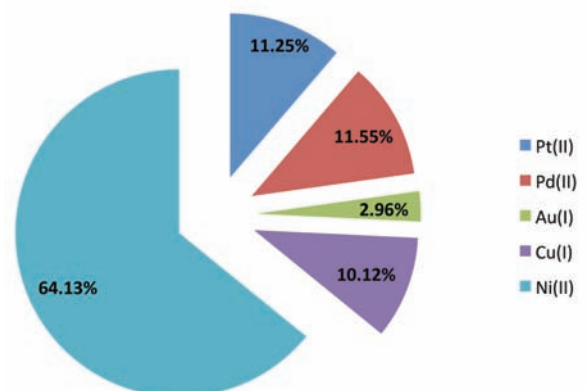


Figure 7—Precious and base metals distribution loading (wt %) on activated carbon after 10 consecutive loadings from a fresh synthetic solution (adsorbent concentration: 10 g/l; temperature: 25°C; Cu: 10 ppm; Ni: 10 ppm; pH: 9.5; CN: 132 ppm; SCN: 100 ppm; Pt: 0.86 ppm; Pd: 10ppm; Au: 0.17 ppm; rotational rate: 105 r/min)

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The pre-treatment step was conducted outside the column by stirring the activated carbon in glass beakers for 30 minutes in 40 ml of NaCN and NaOH solution at room temperature. After the pre-treatment, the carbon was separated from the solution by decanting, and the excessive solution removed by blotting with filter paper. The carbon was then dropped into the glass column containing 0.5 BV of eluant at the elution temperature. The starting time for the elution was taken as the moment when flow of eluant was introduced. ICP-AES were used for all elution experiments.

Elution results

Figure 8 illustrates the elution of platinum, palladium, and gold from activated carbon with distilled water at 80°C after pre-treatment with a caustic cyanide solution as outlined in the previous section. A typical elution profile can be seen for platinum and palladium with a peak in concentration around 2 BV for both platinum and palladium, indicating fast elution kinetics for both metals. In comparison with platinum and palladium, the elution of gold was found to be significantly slower with less of a pronounced peak than that of platinum and palladium.

The elution of platinum and palladium slows significantly after approximately 4–5 BV, with the concentration of these metals in the eluate approaching zero, indicating that the carbon is either stripped completely or stripped of all elutable species. The gold elution profile, with a broad peak at approximately 5 to 6 BV, indicates that there is still a significant amount of gold on the carbon at 16 BV. This compares reasonably well with the shape of the elution profiles at this temperature found in the literature (Van der Merwe, 1991). Typical industrial gold elution temperatures range from 110–130°C.

As previously been shown in Figure 6, the amount of metal on the carbon affects the rate of adsorption of PGMs onto the carbon. It is for this reason that the adsorption stages of a typical CIP circuit employ a countercurrent configuration, where the barren carbon with a high activity (carbon after elution) is contacted with the tailings stream in the last adsorption stage in order to remove the last trace quantities of gold. Any gold that is not extracted there is lost to the tailings. Therefore, in order to consistently achieve low barren losses, it is important to maintain a low concentration of gold on the carbon in the last adsorption stage, which means that the carbon must always be eluted efficiently. Fleming *et al.* (2011) showed that increasing the amount of gold on the eluted carbon that is recycled to the adsorption section from 0 to 50 g/t resulted in an increase in the soluble losses by 370 per cent.

According to Fleming *et al.* (2011), the upgrading ratio of the precious metals in the solution has a significant impact on the plant performance, and when carefully considered during the design stages can result in important advantages. Increasing the upgrading ratio and lowering the carbon advance rate is beneficial as it reduces the size of the elution and regeneration plants and lowers both capital and operating costs. However, operating the plant at higher gold loadings slows the rate of adsorption of gold cyanide onto carbon, which will result in a larger 'metals in process' (MIP) amount and can potentially increase the gold losses in the barrens solution. It is possible to achieve both high gold

loading on the carbon (7000 g/t) and low barrens (0.002 mg/l) by installing more adsorption tanks. To arrive at an optimum design, a simple trade off-analysis can be made of the once-off capital cost penalty of an extra tank versus the lifetime operating cost benefit of a lower carbon flow to elution and regeneration.

The upgrade ratio or, otherwise stated, the concentration to which the PGMs can be upgraded, depends on two factors, namely the metal loading on the activated carbon achieved during adsorption and the elution recovery. To investigate this, equilibrium adsorption experiments and subsequent elution thereof were conducted. The equilibrium loading on the carbon for Pt and Pd from a solution containing 30 ppm Pt and Pd each were 3436 g/t for Pt and 3624 g/t for Pd. Depending on the elution recovery, the PGM concentrations achieved are shown in Table III.

As with gold elution, the elution temperature is probably the most significant factor. In Figure 9, higher recoveries and a slight shift of the elution profiles towards the left of the graph indicates better elution efficiencies for Pt and Pd at higher temperatures. At 4 BV, a drop in recovery from 90 per cent for both Pt and Pd to approximately 64 per cent and 68 per cent for Pt and Pd respectively is shown when the elution temperature drops from 80°C to 60°C.

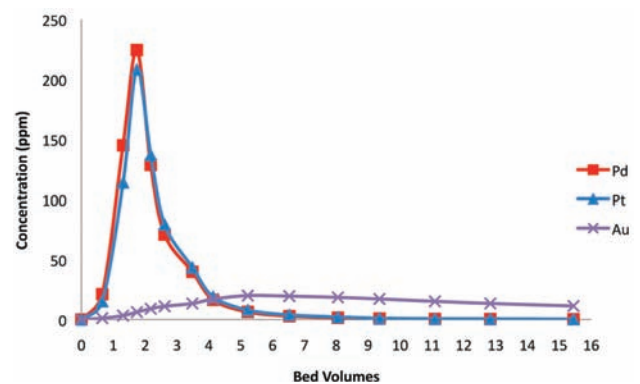


Figure 8—The elution of platinum, palladium, and gold from activated carbon (650 g/t of Pt, Pd and Au each) after pre-treatment with a caustic cyanide solution (2% NaCN, 0.55% NaOH) at an elution temperature of 80°C

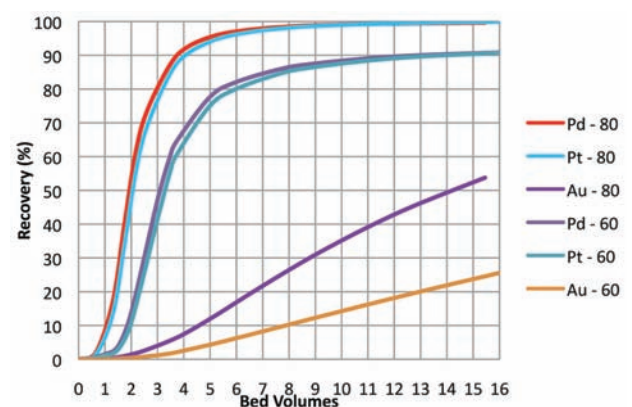


Figure 9—PGM elution recovery curve at 80°C and 60°C (activated carbon loading 650 g/t of Pt, Pd, and Au each after pre-treatment with 2% NaCN and 0.55% NaOH)

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A major operating cost common to elution processes is that of sodium cyanide, and reagent consumption is therefore important. Boshoff (1994) concluded that the feasibility of cyanide-free elution of gold depends largely on the amount of copper loaded on the activated carbon. The higher the Cu loading, the more important cyanide becomes in the pre-treatment step to ensure efficient elution of both copper and gold. This is attributed largely to the difference in adsorption and elution behaviour between the $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$, and $\text{Cu}(\text{CN})_4^{3-}$ complexes in solution. The $\text{Cu}(\text{CN})_2^-$ will load strongly onto the carbon while $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ do not. For the effective elution of copper from activated carbon, both free cyanide concentration and pH need to be sufficiently high to ensure that the complexes are $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$.

A similar effect can be seen for activated carbon loaded with platinum, palladium, and gold cyanide complexes. Figure 10 indicates a significant increase in the concentration peak of the platinum elution profile (indicating better elution of the platinum) as the cyanide in the pre-treatment step is increased from 0 to 0.8 g. A similar result for palladium and gold was found. The likelihood of more than one cyanide complex with different adsorption characteristics, as with the copper cyanide complexes, was therefore investigated. Vorob'ev-Desyatovskii *et al.* (2012) contacted aqueous solutions of $\text{K}_2[\text{Pt}(\text{CN})_4]$ and $\text{K}_2[\text{Pd}(\text{CN})_4]$ with activated carbon and found that at least two platinum compounds and two palladium compounds occurred on the carbon surface. The majority (> 90%) were identified as tetracyanopalladate(II) $\text{Pd}(\text{CN})_4^{2-}$ and the tetracyanoplatinate(II) complex $\text{Pt}(\text{CN})_4^{2-}$. The minor compounds were thought to be possibly $[\text{Pd}(\text{CN})_2]$ and $[\text{Pt}_2(\text{CN})_{10}]^{4-}$, although this is unlikely. According to Monlien *et al.* (2002), the formation of fully pentacoordinated species at the transition state for Pt and Pd does occur. If this is then the case, a shift between the tetra- and the pentacyano complexes with changing cyanide concentration according to Equation [1], as studied by Sharpe (1976), is therefore likely, with the latter adsorbing less strongly onto activated carbon and therefore eluting better.

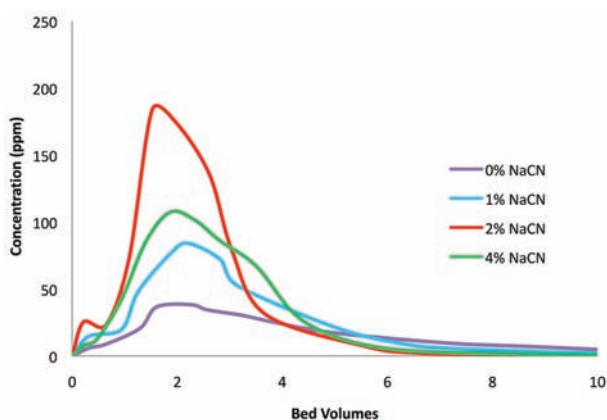
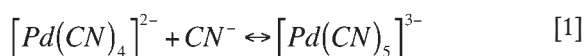


Figure 10—The effect of cyanide pre-treatment on the elution of platinum cyanide (650 g/t of Pt, Pd, and Au each after pretreatment with NaCN as indicated and 0.55% NaOH at 80°C

The occurrence of more than one platinum or palladium cyanide complex on the activated carbon surface, which is influenced with the presence of free cyanide, is therefore deemed likely, but probably only to a fairly small degree when considering the high stability constants ($\log \beta$) of 40 for $[\text{Pt}(\text{CN})_4]^{2-}$ and 51.7 for $[\text{Pd}(\text{CN})_4]^{2-}$ (Monlien *et al.*, 2002)

Figure 10, however, also indicates a decrease in the elution of these metals when the cyanide pre-treatment concentration is increased from 0.8 g to 1.6 g. Both Adams (1991) and Davidson and Bailey (1991) found that an optimum cyanide concentration does exist, and ascribed the decrease in the elution rate at higher cyanide concentrations to the increasing ionic strength.

Analysis of the pre-treatment solution showed trace concentrations of Pt and Pd of 0.05 ppm or 0.05 per cent of the total PGMs for the current carbon loading and pre-treatment conditions.

Figure 11 shows the elution of the PGMs in the presence of copper cyanide complexes. Copper cyanide elutes first with recoveries of 95 per cent in 3 BV, followed by the simultaneous elution of Pd and Pt and with Au eluting last. Cyanide pre-treatment has again been found to have a major influence on the elution of the PGMs as well as of Cu, and this can be explained by the difference in absorbance strength between the different copper complexes, as previously discussed. As in the case of adsorption, however, no additional decrease in the PGM elution efficiency is seen at strong pre-treatment conditions in the presence of Cu, as indicated in Figure 11, which shows similar recovery curves for Pt, Pd, and Au with and without Cu.

Conclusion

PGM adsorption efficiency and recovery were studied as a function of different adsorption parameters such as solution pH, copper concentration, nickel concentration, free cyanide ion concentration, thiocyanate concentration, initial PGM (Pt, Pd, and Au) ion concentration, and activated carbon concentration. It was shown that adsorption rates within the first 60 minutes were very high, and thereafter the adsorption proceeds at a slower rate until a pseudo-steady state was obtained after 72 hours. Among the different adsorption parameters, nickel concentration had the most significant effect on the adsorption process, followed by the adsorbent concentration. Adsorption of Ni was found to proceed at approximately the same rate and with the same recovery as

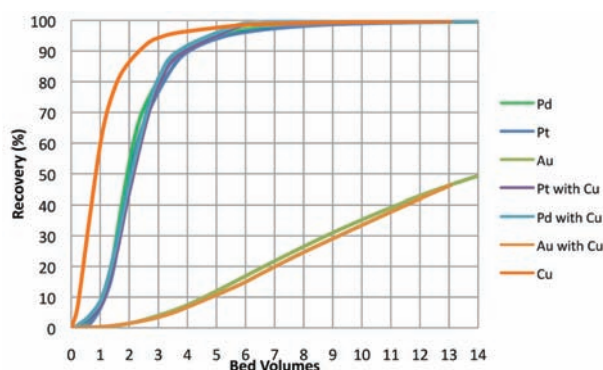


Figure 11—Elution of PGMs and Cu (650 g/t of Pt, Pd, and Au each, 536 g/t Cu after pre-treatment with 2% NaCN and 0.55% NaOH at 80°C

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the precious metals, showing a recovery of approximately 90 per cent in 2 hours. The kinetics of Cu adsorption were slower, with less than 30 per cent recovery after 120 minutes. This suggests that the co-adsorption of Cu can be minimized by shortening the residence time. Adsorption of Fe was found to be less than 5 per cent, while the recovery of Rh was negligibly small. The effect of thiocyanate ion concentration was not as important as the effect of free cyanide ion concentration, but still had some influence.

It was found that platinum and palladium cyanide can be eluted effectively from activated carbon with the AARL method. The elution profiles for platinum and palladium were found to be steeper and to appear earlier than the elution profile of gold, indicating that platinum and palladium will elute before gold. Platinum and palladium elute from activated carbon almost to completion in 4–5 BV at 80°C at the optimum NaCN pre-treatment conditions, while the elution of gold at this temperature is slow. Elution efficiency is improved with higher temperatures, and test work at typical gold CIP elution column temperatures of between 110 and 130°C is still to be completed. The presence of Cu has been found to have no influence on the elution of platinum and palladium at strong pre-treatment conditions, and Cu will primarily elute before the PGMs.

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