

Treatment of Platinum Flotation Products

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A flowsheet has been developed for the production of rich concentrates of precious and non-ferrous metals by a complex treatment of the flotation products from South African platinum-containing chrome ores. The procedure involves: autoclave leaching, roasting, hydrochlorination and precious metal recovery by sorption. Autoclave oxidative leaching of the initial material allows the non-ferrous metals to pass into solution from where they are recovered as a rich sulfide concentrate (> 30% nickel and copper). Recovering the precious metals into solution combines two operations: sinter roasting and hydrochlorination. Roasting destroys the precious metal acid-proof mineral forms. The precious metals are recovered from solution by ion exchange using anionites that are finally burned. The ash from the burning is a concentrate of precious metals (> 75% in total) which are recovered in three forms: ammonium chloroplatinate with purity > 98%, palladium dichlorodiamine with purity > 96%, and a mixture of rhodium, ruthenium and iridium hydrates. The flowsheet uses full water rotation and minimum consumption of reagents, and gives a good recovery of metals to commodity concentrates (nickel > 98%, copper > 80% and precious metals (in total) > 95%).

Most of the primary platinum group metals (pgms) comes from low-sulfide platinum ores (South Africa and the U.S.A) and from sulfide copper-nickel ores (Russian and Canadian deposits). Recent exploration in Russia and elsewhere has resulted in the discovery of some new deposits of platinum-bearing low-sulfide ores. Many existing technologies for treating pgm ore are based on mechanical beneficiation, high-temperature smelting and converting operations, and hydro-metallurgical processing. Therefore, the development of complex hydrometallurgical technology to recover pgms and non-ferrous metals from low-sulfide pgm-bearing ores has considerably simplified the treatment, decreased the operating costs and improved the environmental conditions.

Our investigations involved flotation concentrates of low-sulfide platinum-bearing chrome ores from South Africa. The ore had the compositions shown in the Table. An X-ray microscopy study of the phase composition of the flotation concentrate

showed that nickel is present as pentlandite and copper as chalcopyrite. Iron is present in these minerals and is also present as pyrrhotite and in rock-forming minerals (pyroxene, spinel and talc). Platinum group metals are found as their own sulfides and in mixed sulfide minerals, which are either individual, or associated with non-ferrous metals sulfide minerals and pyrrhotite, see Figure 1. Minor amounts of gold and ferroplatinum in metallic forms have also been discovered.

Based on results of the investigation, the preferred treatment of the flotation concentrate is that shown in the flowsheet, see Figure 2.

Autoclave oxidative leaching (AOL) at a temperature of 150°C and O₂ partial pressure of 1 MPa enables non-ferrous metals to pass into solution selectively. This does not involve precious metal minerals as they are resistant to inorganic acids (1). The effect of sulfuric acid consumption and the process time on the AOL performance were studied. The AOL values were found to be dependent

Chemical Composition of the Initial Concentrates		
Component	Content	
	Concentrate 1, %	Concentrate 2, %
Cu	0.62	2.07
Ni	1.04	3.11
Fe	7.9	12.4
S	1.72	7.09
Mg	9.3	9.45
Al	3.1	3.19
Cr	2.8	1.22
SiO ₂	42.24	38.5
	Concentrate 1, g t ⁻¹	Concentrate 2, g t ⁻¹
Pt	156.0	450
Pd	74.7	310
Rh	26.3	106
Ru	52.7	151
Ir	0.59	37
Os	1.2	26
Au	1.91	4.2
Ag	not analysed	17.4

on the sulfur content in the initial material. For example, during dissolution of concentrate containing a relatively high sulfide content (about 7% S in a sulfide form) the AOL process is carried out in an automatic mode without sulfuric acid addition to the initial slurry. Nickel and copper recoveries are 96 and 80%, respectively, into solution.

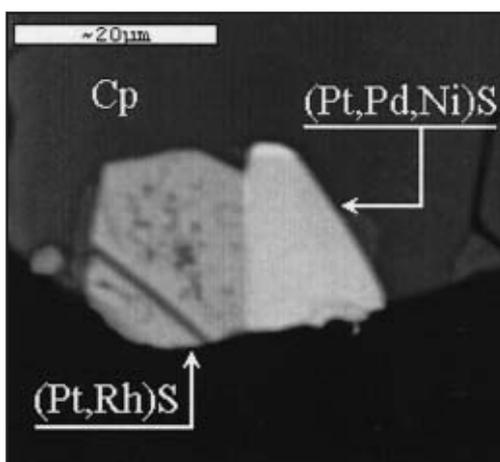


Fig. 1 Optical microscopy shows platinum group element minerals associated with pentlandite and chalcopyrite in reflected electrons (Cp is chalcopyrite)

Leaching of feed with relatively low sulfide content (< 2% S in a sulfide form) is possible under the same conditions, but with acidic additions to the initial slurry (30% of the solids' weight). In this case 94% Ni and 62.5% Cu are recovered into solution. Platinum group metals recoveries into solution are not high for these types of concentrate and are not more than 0.5% for platinum and palladium, and not more than 1.2% for rhodium and ruthenium. The AOL process is considered in (2).

Platinum group metals are present in the insoluble leach residues in natural chalcogenide mineral forms; they do not undergo chemical transformation at the AOL stage. Platinum metals may be recovered by a combination of oxidative roasting and hydrochlorination. At the roasting stage pgm minerals are broken down to produce metallic forms which are then dissolved during hydrochlorination to form pgm complex compounds.

The effect of the roasting temperature and time on the Pt and Pd recovered into the chlorination solution is shown in Figures 3(a) and 3(b). The optimum conditions for oxidative roasting are: temperature 1000°C, time 1 hour, and rate of heating the material 6.5–7.5°C min⁻¹. In order to decrease sulfur dioxide production, a method to change sulfur to sulfate during roasting by adding calcium oxide to the initial feed was tested.

The effects of parameters, such as the type of oxidising agent, HCl concentration, slurry density, and time and sequence of the process on the final hydrochlorination values were studied so that maximum amounts of pgm could be recovered from the sinter. The effects on the pgm recoveries into solution of preliminary grinding before sintering and reduction by hydrazine were estimated. Chlorine gas was the preferred oxidising agent at the sinter hydrochlorination stage rather than hydrogen peroxide or potassium permanganate. The optimal acidity of the slurry for maximum pgm recovery into solution corresponds to an HCl concentration of 220 g l⁻¹, see Figure 4, consistent with industrial practice (3). The platinum metals associates and rhodium, in particular, are sensitive to variations in the HCl concentration. The pgms recovered at the hydrochlorination stage decrease as the initial slurry density grows, see Figure 5. The

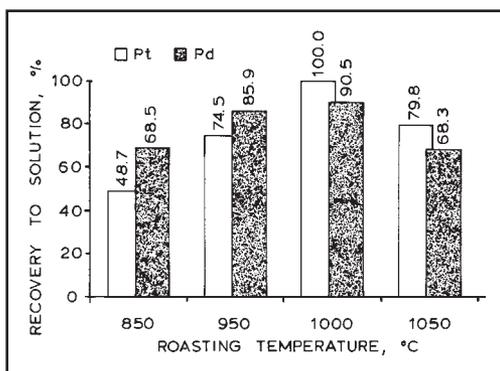


Fig. 3(a) The effect of roasting temperature on platinum and palladium recovery into chlorination solution (roasting time = 2 hours)

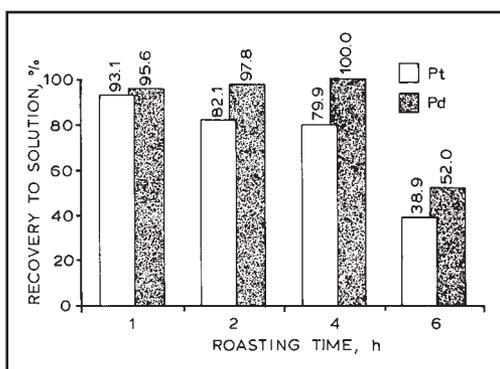


Fig. 3(b) Effect of roasting time on platinum and palladium recovery into chlorination solution (roasting temperature = 1000°C)

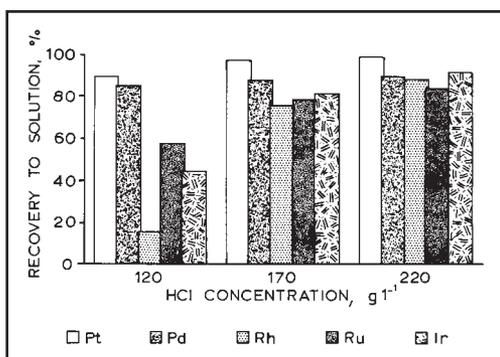


Fig. 4 Platinum metals recoveries into the chlorination solution as a function of HCl concentration (L:S ratio = 10, chlorination time = 2 hours)

maximum drop in recovery is seen with a L:S (liquid:solid) ratio change from 3 to 2. Variations in the slurry density in the range L:S = 3–5 have practically no effect on the platinum metals recov-

eries. When the chlorination time was increased from 2 to 4 hours, there was an increase in the pgms recoveries into solution. In general, platinum metals recoveries increase when the two-stage leaching process is used in a countercurrent mode. During a two-stage leaching process in solutions containing 170 g l⁻¹ HCl, platinum extraction exceeded 99%, while extraction of palladium and platinum metals associates was over 90%.

The platinum metals recoveries as a function of the time and sequence of the chlorination process are given in Figure 6. Sinter grinding and preliminary reduction by hydrazine allow the platinum metals recovered into solution to increase by 5–10% on average, see Figure 7.

Particle size analysis of the final chlorination cakes showed that the size distribution of the platinum metals is in proportion to the size yields. The

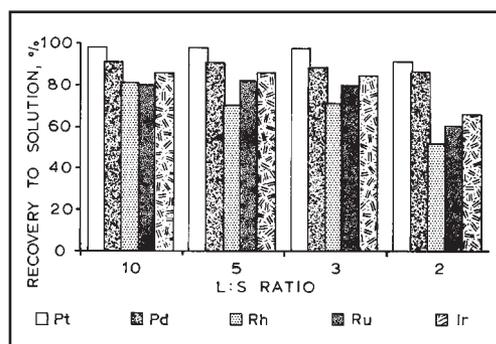


Fig. 5 Platinum metals recoveries into chlorination solution as a function of initial slurry density (170 g l⁻¹ HCl, chlorination time = 2 hours)

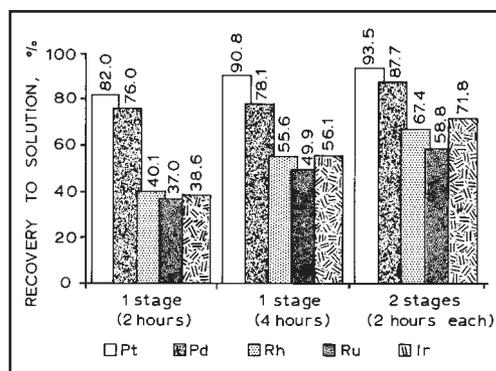


Fig. 6 Effect of the chlorination time on platinum group metals recoveries into solution (120 g l⁻¹ HCl, L:S ratio = 2)

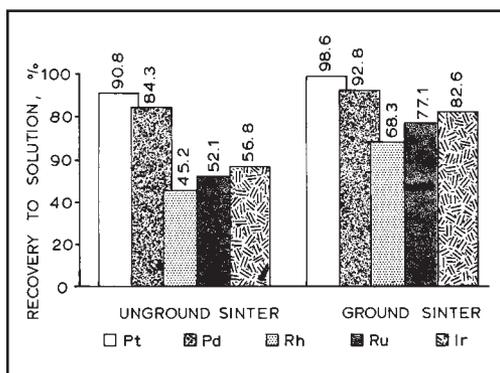


Fig. 7 Effect of sinter grinding on platinum group metals recoveries into solution (220 g l⁻¹ HCl, L:S ratio = 2, chlorination time = 2 hours)

maximum pgms content occurs at a size of ~ 10 μm while the minimum content occurs in the range > 44 μm but < 74 μm. The minor concentration of rare platinum metals (Rh, Ru, Ir) in the ~ 10 μm fraction is noted. Mineralogical analysis of the hydrochlorination cakes, see Figure 8, showed that all the platinum metals are present in acid-soluble forms (intermetallic compounds, dioxides). The incomplete recovery of platinum metals into the chlorination solution may be explained by their isolation by the rock minerals. An additional flotation recovery of platinum metals from the final hydrochlorination cakes enables the production of sufficiently rich concentrates (~ 500 g t⁻¹) with the mass of the initial material decreasing by up to three times. The concentrates may then be

returned to the roasting stage of the flowsheet.

Platinum metals recovery from hydrochlorination solutions was carried out by ion exchange (sorption). Anionite Rossion-11, a porous sorbent based on styrene and divinylbenzene with functional groups of primary, secondary and tertiary amines (-NH₂, =NH, ≡N) groups, characterised by high selectivity towards the pgms, was used as the sorbent. It was found that for maximum amounts of pgms to pass to the sorbent, the HCl concentration in solution should not be higher than 125 g l⁻¹, while the ferric iron concentration should not be more than 15 g l⁻¹. The solution oxidation-reduction potential should be < 800 mV; this is also important to avoid sorbent destruction.

During the ion exchange process, with the rate of solution passing being: 2 volumes of solution to 1 volume of resin per hour, the following residual pgm content in the sorbate was (in mg l⁻¹): platinum < 1; palladium 1–1.5; rhodium < 1; ruthenium 3–4; iridium 1–2. The residual contents correspond to a total pgms recovery of 95 to 98%. However, if the sorbate, containing residual amounts of pgms, is used to prepare hydrochlorination solutions – thus returning pgms to the chlorine leaching process – the pgm recoveries at the ion exchange stage will reach 99.5%.

During the investigations it was found that the optimum ion exchange modes developed using simulated solutions are reproduced in existing technological solutions for all the pgms, except

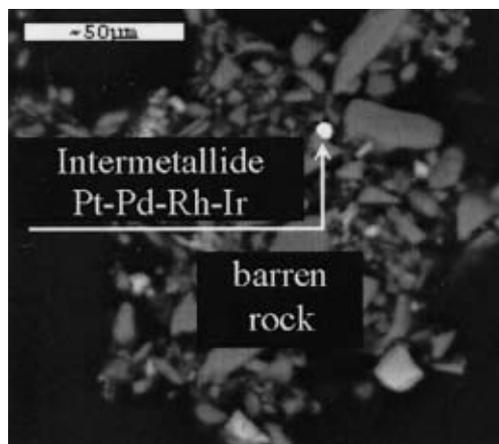
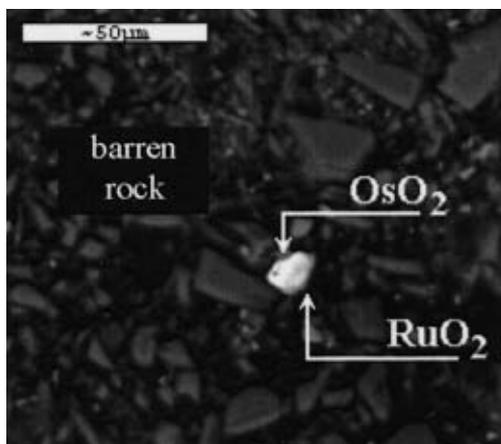


Fig. 8 Platinum group metals and their compounds in the final hydrochlorination cakes

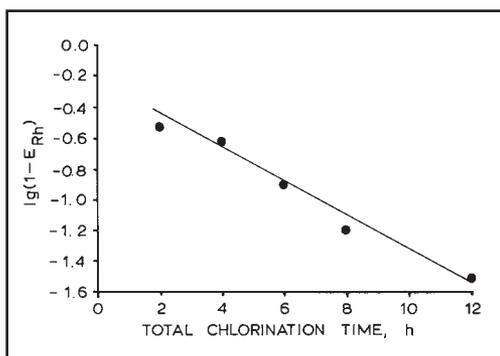


Fig. 9 The degree of rhodium sorption recovery from solutions (E_{Rh}) as a function of the total chlorination time (sinter hydrochlorination and additional treatment of solution)

rhodium. The reasons for the incomplete recovery of rhodium into the sorbent during ion exchange have been determined. Rhodium recovery into solution decreases as the sinter hydrochlorination time reduces due to the production of poorly sorbed forms of rhodium, such as $[\text{RhCl}_6]^{2-}$, $[\text{RhCl}_{6-x}(\text{H}_2\text{O})_x]^{x-3}$, $[\text{RhCl}_{6-x}(\text{H}_2\text{O})_x]^{x-2}$, etc. Based on the chlorination process time of 2 hours the sorption recovery figure is 70.3%. An additional two-hour treatment of the solution by chlorine at 90°C helps to increase rhodium recovery to 76%, while a six-hour treatment increases it to 93.8%. It is also noted that if the six-hour solution is held at 90°C (while mixing), then the free chlorine in solution facilitates rhodium transformation to the most sorbed form, $([\text{RhCl}_6]^{3-})$, and increases rhodium recovery into the sorbent up to 97%, see Figure 9.

The resin produced from the sorption contains pgms and gold in the amount 90 kg of precious metal per tonne of air-dry resin. These studies showed there was the potential for pgm recovery from resin by both combined and selective pgm desorption and sorbent burning.

Burning the preliminary dried resin for 4 hours at 1000°C results in pgm-rich concentrates. The pgm and gold content in the concentrates is 80–85%. The ash yield (pgm concentrate) is 3–6% of the weight of the sorbent feed for burning. Gases, such as CO, CO₂, CH₄, are produced from the burning resin, while nitrogen oxides are formed when the resin is burned in an oxidising atmosphere. These gases require attention before

being vented to the atmosphere.

It was found earlier, that anionites based on vinylpyridine sorb platinum and palladium well from nitrate and chloride solutions. Palladium is easily desorbed from anionite with dilute ammonia solution (5% on NH₃). Technology based on this has been used to separate platinum and palladium from silver nitrate electrolyte at an affinage works since 1994. Electrolytes containing as much as 600 g l⁻¹ silver and 80 g l⁻¹ copper, have undergone purification. The platinum content of the electrolytes is in the range 30–500 mg l⁻¹, and the palladium content is in the range 200–2500 mg l⁻¹. The exchange resin capacity for platinum and palladium together is up to 45 g l⁻¹. Palladium is desorbed from the resin by ammonia solution, precipitating palladium dichlorodiamine salt of purity more than 99% (~ 99.9%) from the palladium strippant. The resin is returned to the sorption. The platinum accumulated in the resin after ammonia flushing needs to be desorbed with thiourea, to precipitate an acid-soluble platinum-palladium concentrate from the strippant (5).

Similar technology has been used since 2000 to process solutions from leached pgm materials. A two-stage pgm sorption recovery from hydrochlorination solutions was developed (Figure 10).

In the first stage Pt and Pd are recovered. Anionite containing pyridine groups has been synthesised for this. The distinctive feature of the anionite is that ammonia can desorb platinum and palladium from it. Quadrivalent platinum is reduced on anionite to bivalent platinum and as a result can be transferred to ammonia solution by desorption. The optimum composition of the resin functional groups and the structure have been determined. After oxidation, ammonia chloroplatinate and palladium dichlorodiamine are precipitated from the ammonia strippant. The anionite capacity is ~ 35 g l⁻¹ for platinum and palladium together.

In the second stage Rh, Ru and Ir are recovered by Rossion-11 anionite. Platinum group metals are desorbed from anionite with hot (60–80°C) thiourea solution. A mixture of Rh, Ru and Ir hydrates is precipitated from the thiourea solution. The iron and non-ferrous metals content of the

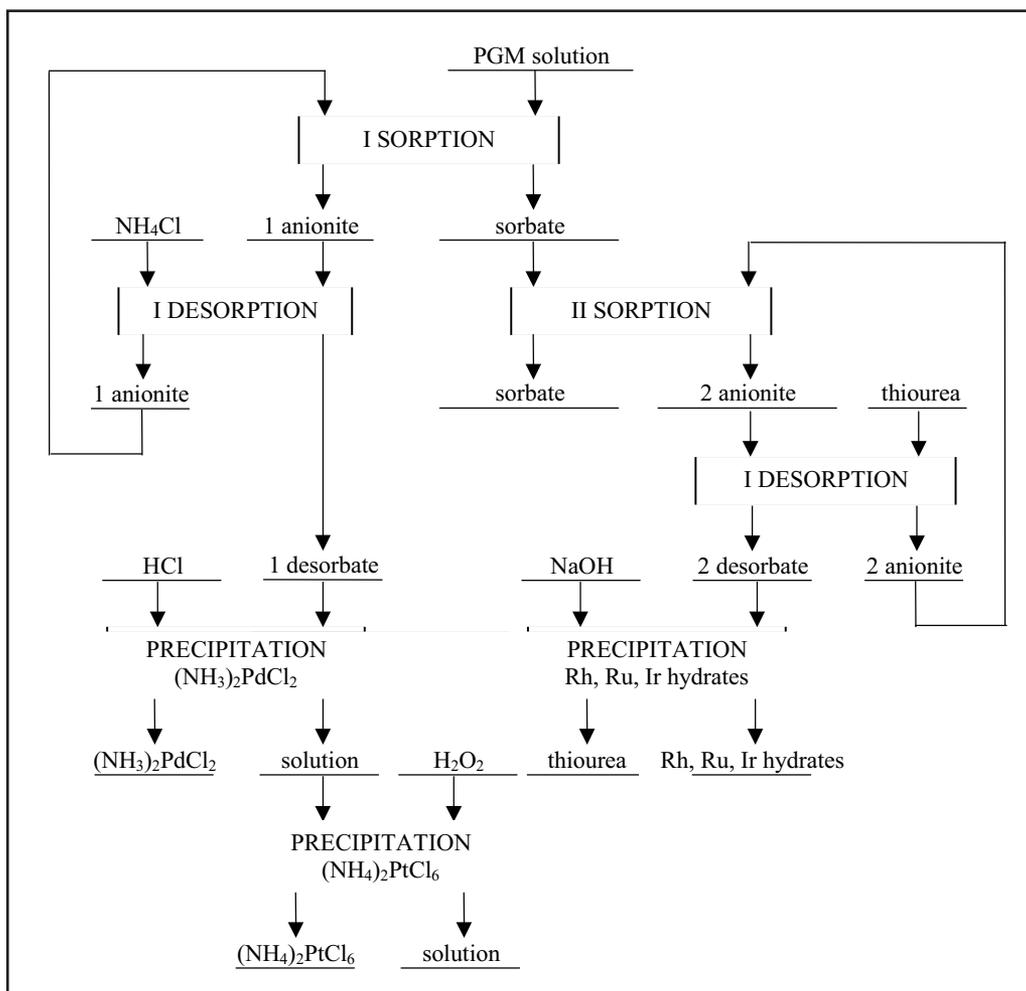


Fig. 10 Two-stage pgm sorption recovery from hydrochlorination solutions

concentrate produced does not exceed 4% of the total (Rh, Ru and Ir).

At the oxidative roasting stage of autoclave leaching the insoluble residue, and during burning the saturated resin, sublimation of volatile osmium and, partly, ruthenium oxides to the gas phase takes place. It is therefore necessary to collect, recover and then separate the products. Methods of collecting osmium tetroxide from roaster gases are employed at existing plants in Russia (4).

Conclusions

A flowsheet for treating flotation concentrates produced from low-sulfide platinum-containing ores has been developed. It provides low con-

sumption of cheap reagents, complete water circulation and gives a high recovery of platinum group metals and non-ferrous metals into rich concentrates. These are then suitable for refining.

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Platinum/Carbon Nanotubes in PEMFCs

Proton exchange membrane fuel cells (PEMFCs) generate electric power efficiently without producing exhaust gases, so are very desirable for use in LEVs or ZEVs (low or zero emission vehicles) and as power sources for small portable electronics. However, achieving minimised metal content with the costly platinum group metals catalysts is one of the challenges to their commercialisation.

Now, researchers at the University of California, Riverside, U.S.A., have investigated increasing Pt utilisation in PEMFCs by using carbon multiwalled nanotubes (MWNTs) as the Pt support (C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon and Y. Yan, *Nano Lett.*, 2004, 4, (2), 345–348; DOI: 10.1021/nl034952p).

MWNTs were grown directly onto C paper by chemical vapour deposition. The Pt catalyst was then electrodeposited onto the MWNTs. The Pt particles had an average diameter of 25 nm (commercial Pt/C catalysts are 2–3 nm). There was good electrical contact between the MWNTs and the C paper and excellent adhesion. The surface area of the MWNT-C paper composite was ~ 80–140 m² g⁻¹ (< 2 m² g⁻¹ for the C paper alone).

A membrane electrode assembly was prepared with two of the composite electrodes and tested in a fuel cell station. Its performance was lower than that of a conventional PEMFC, but its robustness was confirmed. It is suggested that reducing the Pt particle size to ~ 2.5 nm, improving MWNT yield and reducing tube diameter will give C nanotube-based fuel cells of superior performance.

Optical Hydrogen Sensors Using Palladium-Silicon

Hydrogen (H₂) can be detected in several ways but the technique chosen must take into account the conditions of its use, other impurities likely to be present and the physical demands upon it. The methods include semiconductor metal oxides, electrochemical methods, pellistors, palladium and optical means. Response time and the threshold limit are important factors. As H₂ becomes more widely used, reliable detectors able to detect hydrogen before it gets to explosive amounts in air (> 4.65 vol.% H₂) are increasingly important.

Now scientists at the University of California, San Diego, U.S.A., have used optical interferometry to detect H₂ using Pd-coated porous Si (H. Lin, T. Gao, J. Fantini and M. J. Sailor, *Langmuir*, 2004, 20, (12), 5104–5108; DOI: 10.1021/1a04974lu). Thin porous Si films were immersion plated with Pd. On exposure to H₂, the wavelength and inten-

sity of their Fabry-Pérot fringes, obtained from the interferometric reflectance spectrum were simultaneously measured. The intensity of the fringes depends on the reflectivity of the Pd/porous Si composite and their wavelength depends on the refractive index of the Pd film. H₂ expands the Pd lattice and this shifts the optical fringes and decreases the intensity of the reflected light.

The set-up used by the researchers gave a detection limit of H₂ at room temperature of ~ 0.2% (by volume) in nitrogen, with the lowest concentration detected being ~ 0.17%. The response time was a few seconds. This sensor design reliably detects H₂ concentrations well below the explosive limit. The sensor is safe, sensitive, selective, reproducible and can operate at room temperature. However, as CO impedes the adsorption and desorption of H₂, the response time is longer, if CO is present.