The recovery of precious metals from acidic effluents using sodium formate

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Abstract: At Western Platinum Refinery in South Africa, zinc was used for the reduction of the platinum group metals (PGMs) in acidic effluent (palladium filtrate). Owing to the increasing cost of zinc and the risk of zinc pollution, sodium formate was investigated as an alternative reductant. It was found that pH 1.5 was the optimum starting pH for sodium formate reduction. The optimum concentration of sodium formate was found to be 18 g/dm³ at a temperature of approximately 100°C where the process time was 5 hours. The addition of sodium formate increased the pH of the final reaction mixture to approximately pH 4.5. Palladium was the most effectively reduced PGM, exhibiting an average precipitation efficiency of 98%. Difficulty was experienced with the precipitation of platinum (average precipitation efficiency of 47%). The precipitated PGMs were readily dissolved in hydrochloric acid (6 M) and sodium chlorate (2%). A reduction in costs resulted from the discontinuation of the use of zinc for reduction purposes. An additional advantage was that zinc was no longer introduced into the PGM refinery circuits. This effectively reduced the pollution potential of the acidic effluent.

Keywords: Platinum group metals; reduction; sodium formate; zinc pollution

Introduction
Western Platinum Refinery is situated approximately 30 kilometres east of Johannesburg in South Africa and the extraction of the platinum group metals (PGMs) contributes to the economy of the region. The recovery of PGMs from palladium filtrate, an acidic effluent, was previously accomplished by using zinc. The average concentrations of PGMs in palladium filtrate were palladium 158 µg/ml, platinum 88 µg/ml, rhodium 16 µg/ml, ruthenium and iridium both <5 µg/ml.

An alternative reductant was needed because of the increasing cost of zinc and the coprecipitation of zinc with the reduced PGM precipitate. Zinc pollution had become a problem. Kojima et al. (1997) used formic acid or sodium formate heated to 250°C at a pressure of 400 kPa for the reduction of heavy metal ions. The method was used in the presence of sulphide or thiocyanate for the precipitation of heavy metals sulphides. Formic acid or sodium formate was used for the reduction of concentrated PGMs after solvent extraction and from precipitated PGM ammonium salts (Grasso 1981; Hasenpusch 1987; Harris et al. 1993). Sodium formate was therefore chosen to replace zinc in the reduction of PGMs as it had advantages of availability and competitive price. The aim of this study was to investigate the advantages of using sodium formate rather than zinc for the precipitation of PGMs from palladium filtrate at Western Platinum Refinery.

Method
Parameters that were investigated included pH, sodium formate concentration, temperature and time. Thereafter, precipitate flocculation, filtration and dissolution tests were performed. Initial laboratory trials were performed in glass beakers with effluent aliquots of between 0.4 and 1 dm³, which were heated and stirred by means of electrically operated magnetic stirrer hotplates. Chemically pure reagents were used for all the experiments. E-pH diagrams were generated using special software (Roine and Haung, 1989; Haung, 1994.
These diagrams were useful in predicting the behaviour of PGMs at different pH and reduction potentials. A standard calomel electrode (SCE) with a platinum foil electrode (Radiometer) was used to determine reduction potentials in experimental solutions (Stoychevski and Williams, 1992; Wang, 1992; Talati and Ghandi, 1995). Filtration was performed using Buchner flasks and funnels, or a glass Witts apparatus, connected to a vacuum pump (Neuberger). Plant trials were conducted in 10000 dm³ vessels heated by means of steam injection. No mechanical agitation was provided. The vessels were made of glass reinforced vinyl ester resin with conical bottoms fitted with valves. Fume extraction was provided in the lids of these vessels. Precipitation efficiency percentages for each element studied were calculated as follows:

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\% \text{ precipitation efficiency} = \frac{\text{Initial concentration} - \text{Final concentration}}{\text{Initial concentration}} \times 100
\]

A rapid colourimetric test for residual PGMs in solution was developed using potassium iodide and stannous chloride solutions. Hoke (1982); Miyake et al. (1990).

**pH considerations**

To study the effect of pH, a concentration of 30 g/dm³ of sodium formate (added in the crystalline form) was chosen. This was based on previous work (Julsing, 1997), where the reduction of PGMs in alkaline effluents was studied. Initial experiments were thus performed on palladium filtrate using sodium formate at 30 g/dm³ at 100ºC. The initial pH of palladium filtrate was approximately 4. The starting pH levels of the effluents were adjusted using hydrochloric acid. Experiments were carried out on palladium filtrate solution, using a range of pH, (pH 0.7 to pH 2.7), to determine the optimum starting pH for the sodium formate process at 30 g/dm³ and 100ºC.

**Effect of sodium formate addition**

Initial laboratory experiments were performed prior to plant trials. Palladium filtrate was treated with sodium formate, added in the crystalline form (5 g/dm³ to 50 g/dm³), at 100ºC and a starting pH of 1.5. Thereafter, plant trials were performed utilising palladium filtrate, with crystalline sodium formate (at 20 g/dm³, 100ºC and starting pH 1.5) in 3 batches of 8000 dm³. Further plant work was performed on 32 batches of palladium filtrate, (8000 dm³ each) with sodium formate added in various quantities to obtain −100 mV (SCE) in the solution.

**Effect of temperature**

Tests were performed at various temperatures between 20ºC and 100ºC using a starting pH of 1.5 and a sodium formate concentration of 15 g/dm³.

**Effect of time**

After the necessary amount of sodium formate (15 g/dm³) was added to the solution being reduced (the reduction potential was below −100 mV (SCE) at 100ºC), the temperature and agitation was maintained for periods up to a maximum of 19 hours. Samples were taken from the laboratory tests at hourly intervals to determine the effect of time on the reduction of PGMs.

**Precipitate flocculation, filtration and dissolution tests**

Different flocculants were used to determine the optimum performance of flocculation for the reduced PGMs in palladium filtrate. The filtration rates were determined through three grades of Whatman filter paper, namely, 541, 540 and 542. The degree of dissolution in 6 M
hydrochloric acid and sodium chlorate (2%) was also determined by weighing the mass of
the residue after leaching at 70°C.

Results and discussion
pH considerations
The precipitation efficiencies of the PGMs in palladium filtrate increased as the starting pH
increased to pH 1.5. Thereafter the precipitation efficiencies for platinum and rhodium
decreased. The same pattern emerged for silver and copper. However, nickel and iron
showed the opposite trend. This was advantageous since presence of base metals was not
desired in the PGM rich precipitate. Arsenic and selenium were reduced at the same precip-
itation efficiency (80%) for each of the pH levels tested. The presence of arsenic and seleni-
um in the precipitate was not considered a problem since they could be removed by
calcin ing or by distillation from the hydrochloric acid medium using cuprous chloride.
Vogel (1951). Calcining involved heating the material to approximately 700°C so that the
metalloids were driven off as the volatile oxides. A disadvantage of calcining was that pas-
sivation of rhodium, ruthenium and iridium sometimes occurred (Julsing and Toerien,
1996). Palladium filtrate was treated with sodium formate (30 g/dm³) on a laboratory scale.
At starting pH 1.5, the maximum precipitation efficiencies were 98%, 83%, and 82% for,
palladium, platinum and rhodium respectively (see Figure 1).

In a previous study (Julsing, 1997), the PGMs, in reducing alkaline medium, showed the
trend of increasing precipitation efficiencies with decreasing pH. In acidic medium, this
trend was different. A peak of PGM precipitation efficiency was found at a starting pH of
approximately 1.5 with a sharp decrease as the pH decreased below pH 0. Selective photo-
catalytic reductions of PGMs were also successfully performed at pH 3.1 (Kriek et al.,
1995). This fell within the range of pH (1.5 to 4.0) of the sodium formate reduction of PGMs.

Effect of sodium formate addition

Laboratory trials using sodium formate for the reduction of PGMs in palladium filtrate. In
the laboratory trials, palladium exhibited excellent precipitation efficiency (98% at
5 g/dm³ sodium formate concentration); see Figure 2. The reason for this was thought to be
the enhancement of sodium formate reduction properties by finely divided palladium
(Pourbaix, 1966; Dicinoski, 1994).

Figure 1 The effect of starting pH on the reduction of PGMs in palladium filtrate using sodium formate
(30 g/dm³) at 100°C
Platinum and rhodium both showed the greatest precipitation efficiencies in the laboratory trials at 25 g/dm$^3$ sodium formate concentration (90% and 78% respectively). The precipitation of silver showed a similar trend. It was thought that not much benefit would be obtained, in terms of platinum and rhodium precipitation, by using a sodium formate concentration greater than 15 g/dm$^3$.

Copper precipitation increased with increasing sodium formate concentration having a maximum precipitation efficiency of 33% at 25 g/dm$^3$ sodium formate. Nickel precipitation was insignificant (below 2%) throughout the range of sodium formate concentrations (5 g/dm$^3$ to 25 g/dm$^3$).

Zinc was present in the PGM ore, so it could not be completely eliminated from the effluent by the use of sodium formate. In the past, up to 5000 kg per month of zinc was used for reduction of PGMs. By using sodium formate instead of zinc, the zinc content of the effluent was decreased to approximately 50 kg per month. The use of sodium formate decreased the zinc concentration in the final effluent by a two orders of magnitude. This, in turn, significantly reduced the pollution risk from the final effluent.

Lead precipitated to a small extent (7% at 10 g/dm$^3$ sodium formate concentration). This was not problematic since these concentrations of base metals could be tolerated in the refinery circuits. Silver showed a proportional trend (32% to 95%) of precipitation efficiency throughout the range of sodium formate concentration (5 g/dm$^3$ to 25 g/dm$^3$). This was desirable since silver increased the value of the precipitate.

In the laboratory trials, the optimum sodium formate concentration appeared to be approximately 15 g/dm$^3$. There was the possibility, that an increase of sodium formate concentration to between 25 and 30 g/dm$^3$ could be justified by the value of additional rhodium recovered. This would only be valid if the rhodium concentration in the palladium filtrate was greater than 10 µg/ml.

Plant trials using sodium formate for the reduction of PGMs in palladium filtrate. Initial plant trials (8000 dm$^3$) confirmed the trends found in the laboratory. Palladium exhibited consistently good precipitation efficiencies of greater than 90% in all three batches. An encouraging 93% precipitation efficiency was obtained for platinum in the first batch but this declined to 54% for the third batch. It was assumed that this was caused by an increase in the amount of stable platinum complex content in the incoming effluent (Hartley, 1973; Dicinoski, 1994).
Over a period of one month, 32 batches of palladium filtrate (8000 dm$^3$ each) were processed in the plant using between 15 and 25 g/dm$^3$ sodium formate at 100ºC and a starting pH of 1.5. Palladium precipitation efficiencies, using sodium formate, were very high (averages of greater than 97%). This was particularly encouraging for palladium filtrate because the primary constituent was palladium. Silver was also reduced at an average precipitation efficiency of 61%, thus contributing to the commercial value of precipitate. Also advantageous were the low precipitation efficiencies for copper, nickel, iron, lead, aluminium and zinc (34%, 13%, 13%, 14%, 9%, and 18% respectively) which resulted in precipitates having relatively low concentrations of these metals. This improved the grade of the PGMs in the precipitates. On the other hand, the high average levels of arsenic and selenium in the precipitates (45% and 27% respectively) resulted in a need for calcination. The average optimum sodium formate concentration for the reduction of PGMs in palladium filtrate in the plant trials was approximately 18 g/dm$^3$. This produced average PGM precipitation efficiencies as follows: palladium 98%, platinum 47% and rhodium 53%.

Comparison of laboratory and plant trials for palladium filtrate
An interesting feature of the comparison of the laboratory and plant trials for palladium filtrate was the decrease in precipitation efficiencies, in the plant trials, for platinum, palladium, rhodium, silver and arsenic. Opposite trends (increase in precipitation efficiencies in the plant trials) were noted for copper, nickel, iron, lead, aluminium, selenium and zinc. This was not beneficial for the concentration of PGMs because the increased concentration of base metals would effectively lower the concentration of the PGMs. An explanation for this was the fact that in the plant, agitation was provided by steam injection into the effluent being processed, whereas the laboratory trials were performed with the relatively more effective magnetic stirrers. The apparent optimum concentration of sodium formate (18 g/dm$^3$) was less than that found in the previous study, Julsing (1997), where 30 g/dm$^3$ sodium formate (with sodium thiosulphate at 30 g/dm$^3$) was used to recover PGMs from alkaline effluents.

Effect of temperature
It was evident that optimum temperature for the sodium formate reduction of PGMs in palladium filtrate was reached at 100ºC. Palladium could be precipitated to 98% precipitation efficiency at 60ºC. This was anticipated due to palladium’s enhancing effect on the reducing power of sodium formate (Pourbaix, 1966; Dicinoski, 1994). The other PGMs are only precipitated to higher (between 50% and 90%) precipitation efficiencies at 100ºC. This was corroborated by the findings in previous work (Julsing, 1997).

Effect of time
Palladium was efficiently precipitated by sodium formate after 1 hour. Again, this was thought to be due to the catalytic effect that finely divided palladium has on the reducing effect of sodium formate. (Pourbaix, 1966; Dicinoski, 1994). For platinum, the percentage metal remaining in solution becomes almost constant, with respect to time, at approximately 50% of the original concentration. The reason for this was thought to be the existence of a very stable platinum complex that is not reduced by very low (–100 mV SCE at 100ºC) reduction potentials. This complex may be an aceto-complex of platinum formed during a preceding process (Hartley, 1973). A processing time of four hours was required to produce maximum precipitation of the PGMs.

Precipitate flocculation, filtration and dissolution tests
Flocculation. The anionic and neutral flocculants that were tested, produced precipitates that settled quickly (approximately 30 minutes for palladium filtrate treated with 0.032%
flocculant). The cheapest flocculant (Magnafloc 351) was selected. Palladium filtrate treated with sodium formate after 0.032% flocculant addition produced acceptable precipitation rates (Adams et al., 1986). The unflocculated solution did not settle appreciably in the required time of 60 minutes.

**Filtration.** Filtration of the precipitates was easily performed through Whatman filter paper grade 540. Similarly, filtration on the plant scale was carried out without any difficulty. This could be attributed to the absence of any gelatinous type material in the precipitate. The filtration rate was approximately 0.12 dm³ per minute on a 150 mm diameter Buchner funnel.

**Dissolution of precipitates.** All the precipitates from the reduction of PGMs in palladium filtrates were readily soluble in 6 M hydrochloric acid and sodium chlorate (2%) at 70°C, provided that the concentration of damp solids (approximately 20% moisture) was not more than 330 g/dm³ in the acid solution.

**Conclusions**

Sodium formate was an effective reducing agent for the recovery of palladium from the acidic effluent, palladium filtrate. This was advantageous since palladium was the major PGM component of the effluent. Sodium formate was not as effective for the reduction of platinum, where it was suggested that a stable complex of platinum prevented the complete reduction of platinum. The residual platinum was subsequently removed by an electrolytic precipitation method. A starting pH of 1.5 with sodium formate concentration of 18 g/dm³ processed at 100°C proved to be most effective in terms of PGM reduction. Under these conditions, the PGMs were precipitated to a maximum in a processing time of four hours. The precipitated PGMs were easily dissolved in 6 M hydrochloric acid and sodium chlorate (2%) at 70°C.

The replacement of zinc by sodium formate, as a reductant for PGMs, resulted in a cost saving of approximately 53%. It also removed the PGM precipitate contamination factor associated with using a metal reductant. The sodium formate treated effluent contained approximately 100 times less zinc than the effluent treated with zinc. This significantly decreased the pollution risks of discharging this effluent.

**References**


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