1. Introduction

Platinum group metals (Pt, Pd, Rh) are widely used in many applications such as catalyst, jewellery, auto-catalyst, and as demand continues to grow, the need to source these important metals from additional sources such as low grade deposits, industrial wastes, former mine and process tailings will increase. South Africa, the largest producer of platinum group metals, still has more than two thirds of the world's platinum reserves, at the same time it also has millions of tonnes of process tailings resulting from the mining and processing, mainly flotation tailings.

PGMs are usually associated with chromite and has been known since the early 1920s [1,2]. Detail studies of this reef by the following researchers ; McLaren and De Villiers [3], Von Gruenewaldt et al., [4] and Gai [5] has also shown the association of PGMs and chromite. The UG-2 and Merensky ores are the main sources of PGMs in South Africa, the Merensky ore has less chromium compared to the UG-2 known to contain about 10% chromium, meaning that most of the PGMs lost in process tailings such as flotation are contained in chromite gangue [6-15]. In a recent study, the recovery of PGMs from the same tailings by flotation has been reported and the process showed Pt and Pd could be concentrated to over 45 g/t [6].

In this work we performed a dry magnetic separation process to concentrate MgCr₂O₄, concentrating MgCr₂O₄ will improve the grade of Pt and Pd associated with the flotation tailing obtained from UG-2 and Merensky projects to be offered as additional resource.

2. Experimental

2.1 Sample

Flotation tailings samples with a d₅₀ size of 45μm were obtained from UG-2 and Merensky projects in South Africa. Ore from UG-2 mainly contains chromite where PGMs are associated with and report to tailings during flotation. Concentrating chromite by magnetic separation can allow possible recovery of the PGMs into chromite product and further recovered by using NiS–FA process. The content of Pt and Pd in the tailings was 0.7 g/t and 0.2 g/t contained in mainly MgSiO₃ and MgCr₂O₄ minerals. A dry coil magnetic separator with its strength varied from 120 to 240 mT was used to separate the tailings into magnetic, middling and non-magnetic fractions in a two-stage operation. Up to around 2 wt% of the tailings was recovered as magnetic fraction in the final stage with Pt and Pd contents exceeding 42 g/t and 13 g/t respectively with total recovery of about 30% and 34%. About 8 wt% of the tailings reported to the middling section giving Pt and Pd contents at 8.3 g/t and 5.33 g/t with a total recovery of 5.9% and 13.2% respectively. XRD studies of the three fractions from magnetic separation show MgCr₂O₄ and MgSiO₃ as the main phases in the magnetic and middling fractions indicating that Pt and Pd are contained in MgCr₂O₄. The results indicate that a dry magnetic separation process could be used to concentrate Pt in PGM flotation tailings to over 40 g/t and offer as the additional resource for recovering Pt and Pd.

Key Words: Platinum group metals ; Flotation tailing ; Magnetic separation ; Magnetic, Non-magnetic.
A dry coil magnetic (Figure 2) separator was used to separate the tailings sample into three fractions; (1) highly magnetic materials, (2) middling and (3) the non-magnetic fractions. Batch samples of 100 g were dispersed in a plastic tray inclined at 5° to 10° and placed over the coil magnet. A magnetic force or intensity ranging between 120 and 240 mT (milli Tesla) was applied and the samples were evenly dispersed with a hand brush. The magnetic fraction from the first stage separation was subject to the second stage magnetic separation at 120 mT, and the middling fraction from the first stage and obtained a highly magnetic fraction. Each of the three fractions was analyzed for their phases and chemical compositions.

Figure 1 The X-ray diffraction pattern of the PGM tailings sample

Figure 2 (A) Schematic representation of the iron copper coil magnetic separator, connected to a 200V, with an electric supply of 10A and a frequency of 50Hz. For dry fine particles the angle of inclination is small, in this experiment an angle (θ) between 5 and 10° was used. The feed material consists mostly of non-magnetic and magnetic material as indicated in the schematic.

2.3 Pre-concentration by NiS-FA technique

2.3.1 Fire Assay (FA)

For chemical analysis of PGMs, Au etc are usually performed by the traditional fire assay (FA) method [7] using either lead and nickel sulphide. Lead fire assay are used for the collection of Au, Rh, Pt and Pd with the inclusion of silver, and there must be sufficient silver present for the cupellation of the lead button where Au, Pt and Pd are concentrated in the silver bead. The NiS button was prepared as follows: fine tailing sample was mixed with, 20 g of sodium tetraborate, 10 g sodium carbonate, 5 g fine powder of Ni, 5 g SiO₂ and 3 g of S. SiO₂ was preferred because of its greater smelting properties and mixing was done in 100 mL plastic bottle to avoid sample contamination before transferring to fire clay crucible and the mixture was transferred into a pre-heated furnace at 1100°C. The sample was kept in the furnace for over 1 hour. During fusion, major elements are partitioned into the glassy slag, the PGMs are preferentially incorporated into a nickel sulphide (NiS button). When the melt was cooled the NiS button separates from the glassy slag as a clean shiny button.

NiS button was ground into fine powder and transferred to 500 mL glass beaker containing 150 mL of concentrated HCl and heated at 90°C to dissolve all solids.

2.3.2 Tellurium (Te) co-precipitation

Pre-concentration procedures are often necessary prior to determination of the PGMs and in this case, co-precipitation on Te was used as discussed below. The acid solution was diluted with 300 mL of water in a 500 mL beaker. For the Te precipitation, 10 mL of Te (1000 ppm) solution and 14 mL of SnCl₂ (100 g SnCl₂, H₂O dissolved in 150 mL HCl and filled to 500 mL with water) solutions were added and filled to 500 mL with water and stirred constantly with a glass rod. Upon addition of the reducing agent, reduction of Te was observed by blackening of the solution. The solution was heated gently to 80°C for about 1 hour and allowed Te precipitate settle, and was followed by cooling, and then vacuum filtered through mixed cellulose ester filter. The precipitate was then dissolved in solution made of 5 mL of HCl and HNO₃ respectively. Then the solution was analyzed by ICP.

2.3.3 Characterization and chemical analyses

Chemical analysis of both solid and solution samples were obtained by using an Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES, SPS 3000, Seiko instrument Inc, Japan).

3. Results and discussions

3.1 Separation by size classification

The separation by sizing for investigating the distribution of Pt and Pd in the size ranges (+100 µm), (-100+32 µm) and (-32 µm) showed random distribution of both metals in all size fractions. Analytical results of the distribution of Pt, Pd and Cr in all the three size fractions showed no indication of the valuable metals concentrated into one of the size fractions. Concentration of Pt and Pd elements given in Table 2, remained consistently similar to the
original values given in Table 1, indicating that classification of the tailings samples into different sizes could not be recommended in any process development for the recovery of the valuable metals. Characterization by XRD (Figure 3) gave peaks similar to that of original sample (Figure 1), but with shorter peak intensities as compared to Figure 1.

3.2 Magnetic separation

This work was more focused on the concentration of Pt and Pd from PGM flotation tailing sample a mixture of Merensky and UG-2 which has followed the extraction of chromium and PGMs minerals. The feed sample to magnetic separator contained mainly chromite which is strongly magnetic but contains PGMs often associated with base metal sulphides and silica which is weakly magnetic. The application of high magnetic intensity was to maximize the capture of chromite along with PGMs in the magnetic fraction and rejection of the gangue materials. The capturing of magnetic materials with less gangue minerals increased the grade of chromium and the PGMs associated with chromium and base metals. However, because of different sizes small particles of non-magnetic materials become embedded in the large particle simply by mechanical entrainment. It was also observed that entrainment of weakly magnetic particles increased the amount of magnetic fraction which lowers the grade of Pt and Pd in magnetic fraction, so to overcome this problem a second-stage magnetic separation process with low magnetic intensity (120 mT) was applied. In the first-stage of magnetic separation, up to 6 wt% of the material (6g/100g sample) reported to the magnetic fraction and over 5 wt% (5g/100g of sample) of material reporting to the middling fraction. Finally, the treatment of the different fractions by NiS-FA for selective concentration of Pt and Pd from slag was performed. Chemical analysis by ICP and evaluation of results showed 12.5 g/t and 7.3 g/t Pt in the magnetic and middling fractions respectively (Table 3) from below 1 g/t in the original tailings sample. Pd also increased to 1.60 g/t in the magnetic fraction and 1.30 g/t in the middling fraction respectively from 0.2 g/t. This separation was achieved at a magnetic strength of 240 mT.

For further improvement of the grade of Pt and Pd, the magnetic fraction obtained from the first-stage was treated in the second-stage magnetic separation at a magnetic strength of 120 mT to obtain two fractions; magnetic and middling fractions. Chemical analysis and evaluation of results showed that magnetic fraction in the second-stage improved Pt grade to 42 g/t (2 wt% or 2 g/100 g sample) and the Pd grade to 8 g/t for a recovery of 30% and 34% respectively as shown in Table 3. The enhancement factor of 60 on Pt grade was as the results of separation of about 4 g of the middling material from the 6 g magnetic material in first-stage. Total middling weight combined from the first and second stages magnetic separations was 8 wt% (up to 8 g/100 g sample). The X-ray diffraction in Figure 4, indicates that both middling Figure 4(b) and magnetic (Figure 4(c) fractions contain high magnetic material (MgCr2O4) and the d-spacing values calculated from the XRD pattern are 4.78Å(18.35°), 3.65Å(24.35°), 2.99Å(30.15°), 2.59Å(35.50°) and

![Figure 3](image1.png)  
**Figure 3** X-ray diffraction pattern of different size fractions

![Figure 4](image2.png)  
**Figure 4** The XRD patterns ; (a) non-magnetic, (b) middling, (c) magnetic fractions
2.23Å(43.10°) correspond well with given values: 4.80Å(18.35°), 3.19Å(24.35°), 2.69Å(30.15°), 2.52Å(35.50°) and 2.11Å(43.10°).

The slight difference between the experimental values and the reference values could be attributed to impurities in tailings sample including MgO and FeCr₂O₄. However, much higher Pt and Pd contents in the magnetic fraction can be attributed to much lower gangue minerals such as silica when its peak disappears in magnetic fraction as compared to the non-magnetic and middling (As indicated if Figure 4, MgCr₂O₄ and MgSiO₃).

The SEM analysis results clearly identified minerals in the final magnetic concentrate as mainly Mg, Cr, Fe and Si which is in support of the XRD peaks indicating that most of the magnetic material composed of MgCr₂O₄ and the particle sizes of the minerals ranged from minus 10 µm to over 100 µm. Particles were gold coated before being analysed to prevent surface charging and to further produce back scattered electrons (BSE). The production of BSE differs with the minerals average atomic number. Thus higher average atomic number minerals appear brighter than lower average atomic number minerals. For example, most silicates have lower average atomic number and appear dark grey in BSE image. These features can be used as the technique to search Cr and other associated minerals like for PGMs, the BSE images of conventional SEM. Figure 5 shows the Si and Cr with Fe mineral in BSE composition image; it is clear that the Cr particle appears brighter than the other minerals around it.

The NiS button was used to further concentrate Pt and Pd by collecting only PGMs into the NiS button, and the gangue minerals such as MgSiO₃ and MgCr₂O₄ were collected into the slag as indicated in Figure 6. Finally, based on the experimental results a process flow sheet was developed as indicated in Figure 7.

4. Conclusions

From the results discussed throughout this paper, it can be concluded that a dry magnetic separation process could be applied to concentrate Pt and Pd contained in PGMs mine flotation tailings associated with chromite. NiS-FA button procedure was used to further concentrate Pt and Pd before the final analysis by ICP. The observations can be summarized as follows:

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Figure 5  SEM analysis of magnetic particles from dry magnetic separation. Photo A indicates the particle sizes as indicated the smallest particle size less than 10µm and the largest particle size over 100µm and photo B showing mapping results as indicated in the last four photos as Fe, Si, Cr and Mg observed at 1400 magnification 20kV accelerating voltage and a working distance of 12mm.

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Figure 6  X-ray diffraction patterns of slag material after NiS-FA showing MgCr₂O₄ as the main phase.

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Figure 7  Schematic flow sheet of the PGMs (Platinum, Palladium) concentration process using dry magnetic separation process and NiS-FA.
(1) Chemical and XRD studies showed original material contained 0.7 g/t Pt, 0.2 g/t Pd and 5 g/t Rh with MgSiO₃ and MgCr₂O₄ as main mineral phases.

(2) A two-stage magnetic separation process investigated allowed excellent recovery of Pt and Pd. In the first-stage, Pt and Pd grades were improved from <1 g/t to 12.5 and 1.6 g/t respectively in the magnetic fraction using a magnetic strength of 240 mT. The final grades were further improved in the second-stage giving grades of Pt and Pd in the magnetic fractions at 42 and 13.67 g/t respectively using magnetic strength of 120 mT.

(3) Application of the NiS-FA button technique to concentrate Pt and Pd for analysis of the metals to evaluate efficiency of the magnetic separation process produced good results.

Preliminary results in the current work indicated that the sample contains high Rh (5 g/t) and increased to 100 g/t from the magnetic separation process. More work is in progress to evaluate this result. Also tests shall be performed to recover Ni that was used to concentrate PGMs.

References