Investigating the Mineralogy of an Oxidised South African PGM Ore from the Western Limb.

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Abstract: In this paper, the mineralogical characteristics of a weathered Platinum Group Minerals (PGMs) ore of Middle Group (1- 4) was investigated with the main objective of proposing a processing route for the ore. The oxidised PGM ore supplied was 60% passing 710µm and the major elements present were: Cr(27.03%), Fe(20.57%), Si(5.417%), Ca(5.43%), Mg(3.87) and Al(2.17%). The ore was analysed for 4Es (Pt, Pd, Rh and Au) content using fire assaying followed by inductively coupled plasma - optical emission spectrometry. The results indicated that the grades of the 4Es were as follows: Au (0.04ppm), Pd (0.94ppm), Pt (1.98) and Rh (0.32). The Pd content is much lower than that of Pt, indicating Pd remobilization from the weathered zone to the lower zone which reduces the flotation efficiency by changing Pt:Pd ratio. The X-ray diffraction results indicated that the oxidised PGM ore sample was dominated by chromite, quartz, iron oxide minerals such magnesium/ferric iron, trevorite (nickel iron oxide) and secondary minerals such as covellite which is generally found in zones of secondary enrichment (supergene) of copper sulphide deposits. More mineralogical investigation is recommended such as Mineral Liberation Analysis in order to investigate the PGM’s grain size distribution, liberation and their associations.

Keywords: Platinum Group Metals, Middle Group, Weathered ore, Mineralogy, Bushveld Igneous Complex

1. Introduction

Today’s global Platinum Group Metals (PGMs) demand is covered by South African, Russian and Zimbabwean PGMs industries. The world’s largest producer of platinum is known to be South Africa which processed about 110mt in 2018 [1]. South Africa is home to the Bushveld Igneous complex (BIC), which is considered the largest resource for PGMs, with the country’s reserves standing at 63,000mt [2]. The pristine sulphide ores are concentrated through the froth flotation process and recoveries of over 85% of PGMs are achieved. Pristine PGM ores are closely associated with the base metal sulphide such as chalcopyrite, pentlandite, and pyrrhotite hence they are easy to float [3].

The interest in exploring the recovery of PGMs from oxidized PGM ores has been influenced by the fast depletion of sulphide PGM-bearing minerals and over 500 million tonnes resource estimates of oxidized PGM ores which are either unmined, mined, stockpiled or discarded as overburden waste in South Africa and Zimbabwe [4]. The beneficiation of oxidized PGM ores by conventional methods (mainly flotation) achieves less than 50% recoveries [5]. Alternative processing routes which are effective need to be developed for higher recoveries to be achieved and for economic benefits. The poor flotation recoveries are due to surface oxidation of sulphide minerals, and this affect the separation of chalcopyrite from pyrite since sulphide flotation depends on the proportion of hydrophobic and hydrophilic species covering the surfaces. The surfaces of the sulphide minerals start oxidising as soon as they are in contact with oxygen or water, due to electrochemical interactions that occur between sulphide minerals or solution species, affecting their subsequent recovery [6].

Hence, there exists a need to develop alternative processing techniques that can treat low grade and non-sulphide ores economically. Different workers have attributed the poor flotation response in oxidized PGMs ores to several factors such as high contents of naturally floating gangue such as talc, chlorite and aluminosilicates, a lack of base metal sulphide
association with PGMs and the Pd remobilization which reduces the flotation efficiency by changing Pt:Pd ratio, an important metric in the flotation of PGM ores [7]. Processing these ores by conventional flotation techniques typically results in very poor recoveries, therefore various hydrometallurgical, pyrometallurgical, and future technologies may provide alternate solutions. This, however, negates the fact that for some of the BIC operations treating pristine ore, the infrastructure of flotation concentrators are already in place and therefore it is viable to explore alternative flotation reagent schemes in an effort to improve Platinum Group element (PGE) recovery when oxidised ore is processed. Little work has been done to quantitatively relate the surface oxidation to flotation performance which makes it inherently difficult for processing plants to optimise flotation conditions for oxidised ores. There is mineralogical contrast which has important implications for potential processing. This project focuses on the characterisation of the oxidized PGMs ore with the intention of fully understanding the properties of the oxidised PGMs ore and suggesting a processing route.

2. Materials and Methods

2.1 Materials

The ore sample used for this study was sourced from one of the chrome mining companies in Limpopo province, South Africa. The ore was obtained from an open pit mine from different pit depths of the MG (1-4) seam.

2.2 Sample characterisation

2.2.1 Particle size distribution of MG (1-4) sample

The as received sample was homogenised and split into representative samples of 1kgs. One of the samples was screened into size fractions according to the screen sizes listed below to determine the particle size distribution (PSD). The screen sizes that were used are 710, 500, 355, 212, 150 and 75μm.

2.2.2 Chemical composition of MG (1-4) seams.

The chemical composition of the sample as received was determined using an X-Ray fluorescence spectrometer (XRF). The sample was pulverized to < 75 microns then placed in an oven to take off all the moisture for about 30 minutes at 100°C. The powder was mixed with a binder then pelletized prior to analysis. The sample was analysed under vacuum using the XRF Rigaku ZSX Primus II equipped with EZScan software.

Fire assaying method was used to determine the amount of 4Es present in the oxidised PGMs ore. The appropriate amount (300-400g) of a sample was weighed on an analytical balance, mixed with a collection nickel sulphide flux to a homogeneous state (uniform colour) and loaded into a fusion furnace at 1150°C for 50 minutes. The crucible was taken out of the furnace and allowed to cool down. Two phases were formed: a silicate slag and a nickel sulphide (NiS) phase which contained all the 4Es. The NiS button, after being hammered into a form of a cube, was loaded into a cupellation furnace at 1 000°C for an hour. The NiS was absorbed by the cupel and some was oxidized because of the presence of atmospheric oxygen in the furnace. When the cupellation was complete, the PGMs & Au and Ag (added as silver nitrate) prill was left on a hollow surface of the cupel. After the cupellation stage, the silver, PGMs and Au were transferred into a multi-hole cupel and loaded into a higher temperature (1100°C) furnace for 1.5 hours. It was then removed, left to cool and weighed on the analytical balance and a simple calculation was done to determine the PGM concentrations. The detection limit was 0.28 g/t. The PGMs and Au held by the silver prill were transferred into a borosilicate glass tube and aqua regia was added. The tube was then sealed and transferred into a metal housing and placed into a dissolution oven. The tube with aqua regia solution and PGMs and Au were left to dissolve in an oven at 220°C for eight hours. The tube was popped and the solution of PGM and Au were transferred into a volumetric flask, an internal standard was added, made up to volume and assayed on the ICP-OES or ICP-MS, depending on the grade and required detection levels.

2.2.2 Mineralogical composition, surface morphology and mineral distribution of the MG (1-4) seams.

The X-Ray Diffraction (XRD) was used to determine the mineralogical phases present in the sample. The as-received sample was well pulverized to < 75 microns and placed on the aluminium sample holder. After sample preparation, the sample was scanned using Rigaku Ultima IV in the range of 5 to 90 degrees at a scanning rate of 0.5 deg/min with a step width of 0.01 degrees while the source of energy was copper (λ= 1.5) set at a potential 40 KV of and intensity of 30 mA.
After analysis, the generated spectrum was analysed using Integration X-ray powder diffraction (PDXL) software to identify phases that were present.

The surface morphology and the mineral distribution was determined using a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). The sample was characterized in the form of powder to see the morphology. It was coated prior to analysis to make it conductive. Images were collected using a secondary electron detector working under nano-space using the vega3 software while the chemical composition on selected spot point was done using EDS equipped with Integrated Calibration and Application (INCA) software.

3. Results and discussion
3.2 Particle size distribution of the as received MG (1-4) sample

The PSD of the as received sample, an oxidised PGM ore was conducted and the results are shown in Fig. 1. The PSD of the sample was 60% passing 800µm. The sample received is a bit coarse and milling to finer sizes prior to flotation is required. The coarse particles present the greatest flotation rate and lowest recovery and separation efficiency [8].

![Particle size distribution of the as-received sample](image)

**Fig. 1: Particle size distribution of the as-received sample**

3.2 Chemical composition of the MG (1-4) seams.

The XRF was conducted to determine the elemental composition of the as received sample and the results are shown in Table 1. No PGMs were identified due to low concentrations but the following base metals were identified: Nickel and Cobalt. The major elements present are Cr (27.03%), Fe (20.57%) and Si (5.41%). Gravity concentration is recommended prior to flotation to remove the chromite as it is in abundance. The results obtained agree with the results found by [9]. The ore was analysed for 4Es at Mintek using fire assaying and the ICP-OES characterization technique and it was found that the ore is low-grade as observed in Table 2. The Pd content is much lower than Pt, indicating Pd remobilization from the weathered zone to the lower zone which might reduce the flotation efficiency by changing Pt: Pd ratio.
Table 1: Chemical Composition of the MG (1-4)

<table>
<thead>
<tr>
<th>Component</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Co</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
<th>Ga</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass%W</td>
<td>0.01</td>
<td>3.87</td>
<td>2.17</td>
<td>5.41</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>5.43</td>
<td>0.33</td>
<td>0.02</td>
<td>27.03</td>
<td>0.17</td>
<td>20.57</td>
<td>0.12</td>
<td>0.07</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Fire assaying Results

<table>
<thead>
<tr>
<th>Element</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1.98</td>
</tr>
<tr>
<td>Pd</td>
<td>0.94</td>
</tr>
<tr>
<td>Rh</td>
<td>0.32</td>
</tr>
<tr>
<td>Au</td>
<td>0.04</td>
</tr>
<tr>
<td>Total</td>
<td>3.28</td>
</tr>
</tbody>
</table>

3.3 Mineralogical composition, surface morphology and mineral distribution of the MG 1-4 seam.

The sample was analysed by XRD for mineralogical composition and the results are shown in Fig. 2. The results indicated that the oxidised PGM ore sample was dominated by chromite, quartz, iron oxide minerals such magnesium/ferric iron, trevorite (nickel iron oxide) and secondary minerals such as covellite which is generally found in zones of secondary enrichment (supergene) of copper sulphide deposits. It is commonly found as coatings on chalcopyrite, chalcocite, bornite, enargite, pyrite, and other sulphides. It often occurs as pseudomorphic replacements of other minerals [9]. The presence of alteration minerals such as iron oxyhydroxide (FeOOH), copper oxide which occurred in minor quantities was identified and they confirmed that the ore sample studied was a non-sulphide ore and hence could not be efficiently beneficiated by conventional xanthate flotation. The SEM-EDS analysis was performed on the sample and the micrograph is presented in Fig.3 while the EDS is presented in Table 3 showing the chemical composition of the spectrums (A, B, C, D and E). The SEM results correspond with the XRD results. There are significant amounts of chromite, quartz and alteration minerals; such as magnesium iron oxide, nickel iron oxide and covellite. The oxidised PGM ore supplied was 60% passing 800µm size fractions contains more liberated chromite grains, although there are some chromite grains that are still locked in silicates. This supports the reason why most plants are normally milling up to P95 of -0.425mm because at this stage the chromite starts to get liberated [10].

![Fig. 2: Mineral composition of the MG (1-4) sample](image-url)
Fig 3: Micrograph of the As-received sample

Table: 3 Chemical Composition of the points Figure 3

| Point | Mg  | Na  | Al  | Si  | Ti  | Cr  | Fe  | Ni  | Zn  | Pt  | Cu  | Pb  | Cl  | O   | Co  | Ca  | Possible Phases                          |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------------------------------------------|
| A     | 8.05| 8.65| 1.25| 0.37| 28.35| 14.67| 0.07| 0.02| 0.11| 0.07| 0.02| 0.11| 34.99|     | Magnesium iron oxide, Aluminium oxide, Iron oxide, Titanium Oxide |
| B     | 9.31| 0.58| 32.73| 12.02| 10.22| 0.02 |     |     |     |     |     |     | 41.06| 0.18|     | Quartz, copper oxide, Chromite            |
| C     | 15.32| 19.47| 15.64| 1.44| 0.09|     |     |     |     |     |     | 0.15| 45.73| 0.13|     | Nickel Iron oxide,                         |
| D     | 12.36| 1.42| 1.73| 29.0| 0.68| 5.12| 0.13| 0.09| 0.06|     |     | 46.59| 0.03| 0.67|     | Quartz, Pyrite                             |
| E     | 15.61| 7.40| 26.80|     |     |     |     |     |     |     |     | 1.66| 47.71| 0.82|     | Aluminium oxide, Magnesium iron oxide      |
Conclusion

The body of work presented in this paper shows strong evidence that the PGM ore studied is weathered ore. The mineralogical study done on material showed oxidation and weathering as the probable causes of the low metallurgical performance of the ore. The results indicated there is an abundance of host minerals showing iron oxides minerals such as magnesium/ferric iron, trevorite (nickel iron oxide) and secondary minerals such as covellite which is generally found in zones of secondary enrichment (Supergene) of copper sulphide. The deposit has abundant amount of chromite and quartz. The fire assaying results indicated that the ore is low-grade and the Pd content is much lower than Pt, indicating Pd remobilization from the weathered zone to the lower zone which reduces the flotation efficiency by changing Pt:Pd ratio. More mineralogical investigation is recommended such as Mineral Liberation Analysis (MLA) to investigate the PGMs grain size distribution, their liberation and association.

Acknowledgements

The authors would want to thank the University of Johannesburg and the National Research Foundation of South Africa [Grant number 132291] for the financial support of this project.

References