Characterization of PGMs-Bearing Chromite Plant Tailings

Nomso Baloyi1; Willie Nheta1; and Vusumuzi Sibanda2

Abstract—Fine chromite plant tailings originating from the processing of the Middle Group (MG)-1/2 were characterized using X-ray fluorescence, X-ray diffraction, and scanning electron microscopy. This investigation was performed to address the knowledge gap concerning low recoveries and poor grades of Platinum Group Minerals (PGMs) during the flotation process and recommend a suitable pretreatment of chromite tailings before flotation. The chemical analysis of the sample indicates a high content of Cr, Fe, Si, Al, and Mg as a sign of the presence of chromite, albrite, enstatite, chlorite, talc, mica, and quartz, as confirmed by the mineralogical analysis. The morphological analysis revealed that most silicate minerals contained in the used chromite tailings are typical products of the alteration of nesosilicates into weathered phyllosilicates. Phyllosilicates are characterized by the detrimental effects of coating PGMs bearing minerals and lead to low recovery and poor grade since they hinder collector adsorption on the PGMs bearing mineral surface. Thus, the attrition of coated PGMs bearing minerals before flotation can be recommended.

Keywords— Alteration minerals; Platinum group minerals; Platinum group metals; Phyllosilicates.

I. INTRODUCTION

The Lower Group–Middle Group (LG-MG) chromitite layer is one of the major layers of the critical zone in the Bushveld Complex (BC). Due to the comparatively large Cr content, it has significant economic implications, especially on the LG-6, which is the thickest chromitite layer of the Bushveld Complex (BC) (0.90 to 1.20 m thick) [1] - [3]. This layer is expanded across the entire western limb and is mined in both the western and eastern limbs of the BC. For many years, a potential occurrence of PGM-bearing minerals has been recognized in the BC in the chromite layers [4]. It should be noted that, apart from the UG2, Merensky Reef and the platreef are characterized by important and economically exploitable Platinum group elements (PGE), or PGE-bearing minerals (5-10 g/t). However, several investigations have demonstrated that PGEs can be also found in the LG and MG chromitite layers in a concentration varying from 0.5 to 3 g/t and are largely entrapped between the chromite grains [5], [2], [6] - [8]. Hence, the LG layer (see Fig. 1) is one of the world’s largest unexplored resources of platinum. However, the grade of PGMs in the main chromite beds is too low to be able to economically beneficiate and extract PGMs as sole valuable materials [7], [9]. The identified PGM grouping is characterized by a high proportion of sulfides PGEs associated with including a considerable amount of malanite where variable proportions of sulfide arsenides and Pt alloyed with Fe are found together. Nowadays, several researchers have been initiated to explore the LG and MG layers for both chromite and PGEs beneficiation. Problems associated with small grain sizes of PGEs in the LG and MG layers render the process challenging. During the beneficiation of Chromite from these ores, their tailing products are characterized by the presence of an important amount of silicate materials where PGEs are found and can be economically recovered. It has been demonstrated from previous studies that tailings dump of the chromium mines in the BC contains close to 400000 oz of PGEs, to which about 38000 oz are added annually [10].

Nonetheless, some chromite tailings are being treated for PGMs and chromite recovery [11]. The plant’s design and operations were initially based on normal PGM methods used to treat traditional Upper Group 2 (UG2) PGMs reefs. Traditional chromite reefs (LG and MG reefs) respond differently during flotation [9]. This has provided some unique hurdles in the recovery of PGMs from typical chromite reefs [12]. Recently, to the best of efforts consented by Sylvania Platinum Ltd, they managed to produce sellable PGMs, and chromite concentrates while working on chromite dumps generated from the LG-6 and MG-1/2 chromitites layers.

With the advancement of extraction processes, it is not uncommon for tailings to be reprocessed using proven ways to recover the remaining valuable minerals, provided that market conditions are favorable at the time [4]. The recovery of PGMs concentrated from typical chrome producers’ tailings streams and dams has sparked renewed attention in recent years. This is reflected in the number of new plants built or in the planning stages. Sylvania Platinum Limited and Jubilee Metals Group are currently focused on the re-treatment of PGM-rich chrome tailings materials from mines[13]. [2]. Fig. 2 is a schematic flow sheet of the ore processing operation implemented at Sylvania Platinum Limited. Chromite is concentrated by gravity separation and at the later stage, chromite tailings are floated for the recovery of PGMs. However, recovering PGMs from such material through flotation leads to a non-optimized concentration process. A

Willie Nheta1 is with the Department of Extraction Metallurgy, and the Minerals Processing Research Centre (MPTRC), University of Johannesburg 44 Nind St, Doornfontein, Johannesburg, 2028.

Nomso Baloyi1 is with the Department of Extraction Metallurgy, and the Minerals Processing Research Centre (MPTRC), University of Johannesburg 44 Nind St, Doornfontein, Johannesburg, 2028.

Vusumuzi Sibanda2 is with the School of Chemical and Metallurgical Engineering, The University of the Witwatersrand 1 Jan Smuts Ave, Braamfontein, Johannesburg, 2017.

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deep characterization of tailing generated during the beneficiation of Chromite is required to be able to understand the implication of different mineralogical structures towards a performant flotation of PGMs. Hence, this study aims to fully characterize the chrome tailings using a bulk chemistry (X-ray fluorescence spectrometer (XRF) and Inductive coupled plasma mass spectrometry (ICP-MS)), X-ray diffraction (XRD), Scanning electron microscopy-energy dispersive X-ray (SEM-EDS) analysis, utilizing mineralogical data as a source of knowledge to enhance PGMs during the beneficiation treatment process into a product of marketable grade.

Experimental

A. Particle size distribution (PSD) analyzer

The PSD was determined using the Microtrac S3500 particle size analyzer with a measuring range from 20 nm to 2 mm. Tri-Laser Technology utilizes angular measurement of scattered light through a full 180° angular range with three lasers and two detector arrays. The analysis of scattered light for particle size determination employs an i-Wie angular scattering theory. About 2 grams of the sample were well dispersed in the deionized water before analysis, then poured into the sample delivery controller incorporated into the instrument, in which the particles are suspended and de-agglomerated by ultrasonic waves and then pumped through the measuring cell where they are illuminated by a laser beam. The direction and intensity of the scattered light is measured by suitably arranged detectors. The Microtrac Flex 10.6.1 software was used to measure the physical effect and translate it into the distribution of particles by size. The results were viewed on a computer monitor and are expressed as a logarithmic S curve of cumulative % mass passing vs. particle size in μm.

B. X-ray fluorescence spectrometer (XRF)

The chromite tailing samples were measured for major and minor elements using a 4kW wavelength dispersive X-ray fluorescence (WDXRF) spectrometer Rigaku ZSX Primus II. XRF is fitted with a Rh X-ray tube to produce X-rays and a scintillation counter (SC) and flow proportional counter (F-PC) detectors. XRF is equipped with the "SQX" standardless fundamental parameters software (FP) analysis program. FP method is a program to make qualitative analysis and calculate semi-quantitative analysis values without using standard samples. The sample was pre-dried, and about 10 g of the sample was mixed with the Sasol wax and milled to make the sample grains small and uniform. The sample was placed in an aluminum cup and applied 20 tons of pressure using a hydraulic press.

C. X-ray Diffractometer (XRD)

The mineralogical composition of chromite tailings was characterized by XRD. A sample was finely milled and placed on a glass sample holder. XRD measurements were performed by using a Rigaku Ultima IV diffractometer, equipment with a copper anode (Cu-Kα) radiation source. Equipment was set at 40 kV and 30 mA in the continuous-scan mode of 5 and 90° (2θ) with a step of 0.02° and a speed scan of 1.5 deg/min. Mineralogy data were predicted using the PDXL software and reference compounds from the International Centre for Diffraction Data (ICDD).

D. Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX)

The as-received sample was resin mounted and polished, and a thin layer of graphite was deposited on the surface using a sputter coater machine. Scanning electron microscopy (SEM) analyses were performed using Tescan Vega-3 XMU.
SEM fully integrated with Oxford X-Max EDS. The identification of minerals and grains was performed using Backscattered electron (BSE) images using an angle selective backscattered (AsB) detector at an acceleration voltage of 20 kV with a sample current of 157 pA, and an optimized working distance of 15 mm. Pure Cu metal was analyzed occasionally to ensure that detector drift on the ED detector was correct. The distribution of the phase minerals in the bulk sample was qualitatively confirmed using INCA software from Oxford. The spectra were collected for 60 s, and element peaks were identified.

E. Inductively coupled plasma mass spectrometry (ICP-MS)

Chemical analysis of PGMs was performed by the traditional fire assay (FA) method using nickel sulfide (NiS). The NiS button was prepared by mixing a fine chrome tailing sample in a polythene bag with 120 g of Borax, 60 g of sodium carbonate, 2 g of Nickel powder, 10 g silica, and 2 g of sulfur powder. The polythene bag was transferred to a fire clay crucible and fused in a muffle furnace at 1100°C for an hour for 1h30. The melt was then poured into an iron mold and allowed to cool. If fusion was not satisfactory i.e., when a nice coherent bead was not obtained, the slag and the button was fused again. The NiS button was cleaned with a brush (by removing any slag material adhering to it), pulverized and transferred to a 500 ml glass beaker, and covered with a watch glass, 100 ml of conc. HCl was added, and the beaker was heated on a hotplate at 150°C until complete dissolution of the NiS. Complete dissolution occurred when about 50ml of the solution was evaporated. More acid (about 15ml) of HCl to ensure complete dissolution and 50ml of distilled water was added and the solution was heated to boiling on a Bunsen burner. To the boiling solution, 2 ml of 1000 mg/ml Te and 5 ml of 20% SnCl₂ (freshly prepared were slowly added with constant stirring until a black turbid precipitate was obtained. The solution was left on a hotplate at 50°C for at least 2 hours until complete coagulation of the Te-precipitate takes place, giving a clear solution. The solution was cooled, and vacuum filtered. The filter paper (45µm membrane filter) along with the Te-precipitate (gold telluride, TePtCl₄, TePdCl₄, etc.) was transferred to a 100 ml beaker and dissolved in 2 ml of freshly prepared HCl and 6ml of concentrated hydrogen peroxide by heating at 150°C for 5 minutes.

The filter paper was then discarded, and heating of the sample solution continued until a clear solution was achieved. If undissolved particles were present, a further 2 ml of HCl was added and heated until a clear solution was obtained. The solution was cooled and quantitatively transferred to a 50 ml volumetric flask, 5 ml of 0.2 mg/l Cd and Tl solution was added for internal standardization, and the volume was made up to 50 ml. The solution was then analyzed using PerkinElmer NexION 300X ICP-MS for the determination of PGMs. The instrument was calibrated using standards Pt, Pd, Rh, Ru, Ir, and Au. 0.1, 0.05, 1.5, and 10 µg/L were prepared from 100 µg/L NIST traceable stock standards, purchased from De Bruyn Spectroscopic solutions. The instrument calibration curve produced a linear regression line of 0.999 (Instrument response against concentration) which was used to determine the concentrations of the PGMs.

III. RESULTS AND DISCUSSION

A. Particle size distribution (PSD)

The PSD of the sample was determined using a Macrotrac instrument. The analysis provides the qualitative result of particle distribution, as displayed in Fig. 3. The results revealed that the sample is characterized by 80% passing < 38µm particles.

![Fig. 3 PSD of as received sample “chromite tailings.”](image)

As demonstrated in Fig 4, the ideal range for better flotation is well-optimized for most plants for sizes ranging between 75 and 105 µm. The comparison of the PSD of the chromite tailing with the required ideal PSD leading to a performance flotation process as represented in Fig 4 revealed that the current sample will float poorly.

The poor flotation performance is related to a lower recovery rate of target minerals and affects the overall recovery and grade. Therefore, the flotation of fines is characterized by a large surface area and low mass resulting in low momentum of particles, low possibility of cohesion “bubble–particle”, hetero-coagulation of particles, high reagent consumption, low or non-selectivity of collector, strong froth stability, high entrainment of fine particles, high viscous pulp, and slimes coating, all of which affect the recovery and grade of the valuable minerals.
B. Bulk Chemistry

The chemical composition of the sample under investigation is summarized in Table 1. The bulk material contains a considerable amount of Cr$_2$O$_3$ (14.28%), Fe$_2$O$_3$ (13.00%), and SiO$_2$ (40.75%), where significant levels of CaO (5.44%), Al$_2$O$_3$ (10.96%), and MgO (8.83%) were also found. Minor impurities consisting of calcium (0.58 wt.%), manganese (0.18 wt.%), sodium (0.11 wt.%), and titanium (0.54 wt.%) were also noted. Calcium and sodium are most likely associated with gangue mineral grains in the form of feldspars and pyroxenes. However, manganese and titanium can all have limited solid substitution in the spinel structure. The mineral deportment analysis was conducted on different size fractions using XRF to determine any existing difference in bulk chemistry based on size. The results indicate that a significant portion of the siliceous material was present in the +75 µm, while Cr$_2$O$_3$ and Fe$_2$O$_3$ were high at lower-size fraction. This suggests that, initially, some of the high silica gangue could be removed by a simple screening procedure without too much of a loss of Cr$_2$O$_3$ and Fe$_2$O$_3$.

C. Separation by size classification

Analyse to represent the distribution of PGE, Au, Ni, Cu, and S in different size fractions were performed and the outcomes are presented in Table 2. Size fraction ranges of (75µm +38µm), (-106µm +75µm), (-150µm +106µm), and (-212µm +150µm) showed a random distribution on both PGEs and BMS. Analytical results of the distribution of PGMs in -38µm fraction showed an indication of the valuable metals concentrated in the size fractions while base metals are randomly distributed.

D. Phase Characterization by XRD

The Characterization results from the XRD analysis displayed in Fig. 5 revealed that the sample is characterized by Chromite, Quartz, Feldspar, Talc, and Enstatite followed by minor contents of chalcopyrite, pentlandite, and pyrrhotite.

E. Mineral abundance of the Chrome plant tailings sample

The results in Table 3 show the abundance of each mineral identified. The mineral abundance weight percentage of chromite, quartz, and enstatite is 38.66, 37.79, and 16.96% respectively.

F. Phase Characterization SEM-EDX

Fig. 6 shows a backscattered-electron image of chromite tailing showing well-liberated chromite grains (light grey – chromite) Silicate grains (darker greys –silicate); black –mounting resin) of chromite tailing. From the analysis of individual element concentration maps, it was possible to assign mineral names to the various grains to produce a classified mineral distribution map for each sample.
Fig. 7 Mapping of chrome tailings

The classified maps for the Chrome tailing samples are shown in Fig. 7. These maps are particularly useful for illustrating the relationship between the texture and mineralogy of different phases present. The results showed that, texturally, the gangue minerals (enstatite) were smaller in grain size than the Chrome. The classified mineral maps may also be used to determine the proportion of the individual minerals. This was achieved by area analysis of each mineral species within the mapped areas. The results in Table 3 show the abundance of each mineral identified. Results from SEM-EDX mapping are shown in Fig. 7, where the BSE image together with selected key element concentration maps is illustrated. Regions of high element correlation between individual maps identify the locations and compositions (qualitative) of the different mineral phases present. For example, chromite grains are indicated by intense regions on the Fe, Cr, and Al distribution maps (=high concentration), while regions of Al, Si, and Ca distributions indicate albite and Si and Mg indicate regions of enstatite. Fig. 7 also shows a composite element map that overlays the concentration data for the elements Fe, Cr, Si, Mg, and Al. In this map, each element was assigned a primary color e.g., Fe= light blue, Cr = purple, Al= blue, Mg= white, Si= green, Na= grey, and Ca= green. Using this color scheme Chrome- rich grains are red orange (mixture of Fe, Cr, and Al) while silicate grains are green in color indicating they are low in Chrome and iron.

G. Discussion

Based on characterization studies from the sieve analysis, most of the particles are less than 38 µm in size, with very little coarse portion of the ore. The results of the size-fraction assay for various size fractions showed that the Cr % increased as the particle's fineness increased, with a maximum of 16.09 % Cr recorded at 38 µm. The Cr: Fe ratio shows a continuous increase in the fineness of the particle, until the particle size of 38 µm (Cr: Fe ratio of 1.20) and then falls with a further increase in the fineness. The decrease in the Cr: Fe ratio can be attributed to the decrease of valuable minerals as the fineness increases. Grade analysis of the chrome tailing was 2.97g/t and different size fraction shows that PGMs were concentrated at finer particle <38 µm was 5.13g/t. The mineral distribution in the chromite tailing sample was analyzed using SEM and EDX. The image observed in SEM, found three different shades of particles in the chromite tailing. The dull or greyish shade particles are combined with silica and other gangue elements. A bit lighter phase shows a greater percentage of chromium and iron indicating the chromite phase. The mapping images demonstrate that chromium and iron were dominating, followed by silicate minerals. The lesser particles are found to be mostly liberated. The XRD pattern for the chromite tailing identified significant mineral phases in the sample, including chromite, albite, enstatite, and quartz. The XRD demonstrates nickel phases that support the presence of nickel in chrome tailing as found in the chemical analysis result.

IV. CONCLUSION

Mineralogical characterization of South African chrome tailings originating from the Middle Group (MG)-1/2 chrome processing plant was undertaken using XRF, XRD, SEM-EDX, and ICP-MS techniques. PSD results confirmed that the sample contains a substation number of ultra fines. The analysis of bulk chemistry revealed that the sample contained Cr2O3 (14.28%), Fe2O3 (13.00%), and SiO2 (40.75%), with major impurities being CaO (5.44%), Al2O3 (10.96%), and MgO (8.83%). The sample mineralogy was dominated by chromite, quartz, feldspar, talc, and enstatite, followed by minor components of chalcopyrite, pentlandite, and pyrrhotite. SEM-EDX and mapping analysis confirmed that the sample mineralogy was dominated by a chrome-rich phase with average chemical compositions (in wt.%) of Cr2O3—38.7, and contaminant phases included siliceous minerals, NaAlSi3O8—37.80, and FeSiO3—17.0m. NiS-FA button finishing with the ICP-MS technique showed that the material contained 1.7 g/t Pt, 0.53 g/t Pd, 0.30 g/t Rh, and 0.44 g/t Ru. The chemical content of the PGMs in the different size fractions showed that the PGMs are more concentrated in the lower fraction of < 38 µm: 2.72 g/t Pt, 0.80 g/t Pd, 0.40 g/t Rh, and 0.68 g/t Ru. Based on the results, a pre-treatment process is ideal for removing ultra-fine phyllosilicate that might result in low recovery and low-grade during froth flotation.

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DATA AVAILABILITY STATEMENT

The data presented in this study are available on request.

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CONFLICTS OF INTEREST

The authors assert that they are not aware of competing financial interests or personal relationships that could have influenced the work reported in this paper.

REFERENCES


A. Author Contributions

Conceptualization, W.N., N.P.B., and V.S; writing—original draft preparation, N.P.B.; writing—review and initial editing, N.P.B and W.N.; supervision, W.N., and V.S.; project administration, W.N.; funding acquisition, W.N. All authors have read and agreed to the published version of the manuscript.