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Pre-treatment of a Hydrocarbon Contaminated Platinum group Minerals Mine Sludge using a Non-ionic Surfactant

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Abstract **-** In South Africa, the Merensky, Upper Group 2 (UG-2), and Platreef are the three primary platinum group mineral (PGM) reefs found in the Bushveld Igneous Complex (BIC). PGM output is now mostly sourced from Platreef and UG-2 reefs. Most of the PGM mines have become highly mechanised, leading to the production of mine sludge contaminated with hydrocarbons. This study investigated the removal of the hydrocarbons using a non-ionic surfactant in preparation for the flotation process. The contaminated mine sludge was characterised for hydrocarbon content, mineralogical and elemental composition. Response Surface Methodology-Box-Behnken (RSM-BBD) design of experiments was used to design the washing experimental runs. The results revealed that the sample contained 9.32g/t of total four elements (Pt, Pd, Rh and Au) with most of the PGMs found in the sulphide form. Chromite and quartz are the common gangue minerals that were found in the sample. Fourier transform infrared spectroscopy showed that there were hydrocarbons present in the sample. The washing experiments showed that Triston-100 (TX-100) can be used to remove hydrocarbons from the contaminated PGMs mine sludge. The optimum washing conditions with a hydrocarbon removal efficiency of 91.86% were found to be 12.25 g/kg surfactant concentration, 150 minutes of washing time and a pH of 12.

Keywords**:** Bushveld Igneous Complex, Mine sludge, Non-ionic surfactant, Flotation, Upper Group 2

1. Introduction

Platinum, palladium, rhodium, ruthenium, iridium and osmium are all members of the platinum-group elements (PGEs). PGEs are some of the rarest metals on the planet; nowadays, the usual PGE concentration in mined ores is between 5 and 15 ppm. These metals exist in nature and have similar physical and chemical characteristics [1]. Around 75% and 50% of the world's platinum and palladium deposits respectively, are found in the Merensky, UG-2 and Platreef of the BIC [2]. Drilling and blasting techniques have been used for a very long time to mine these reefs. There are two types of mining: open-cast and underground mining [3].

In South Africa's more recent mines, mechanised mining is a common mining technique because of the depth of the mines. Machinery that runs "off track" or without tracks is used in the process. Due to its ability to deliver the necessary high-power output, diesel is the fuel that is most frequently utilised for such heavy-duty equipment used in industrial areas, including transportation, mining and construction [3]. Due to the size of such equipment, pipe failure might result in oil leakages, contaminating the mine sludge that is formed from the dust and spray water. The mine sludge is then collected, piled up, and then stored. This contaminated mine sludge needs to be remediated before processing through sulphide froth flotation because the contaminant will cause low platinum group minerals (PGMs) recovery if not removed [4]. Surfactants are used in the washing of hydrocarbon-contaminated ore to remove these pollutants, which presents difficulties when it comes to flotation [5].

The aim of this project is to remediate the hydrocarbons from the PGMs mine sludge using a non-ionic surfactant. The effect of pH, washing time and surfactant concentration on hydrocarbon removal efficiency was investigated based on the Response Surface Methodology (RSM).

2. Materials and Methods

2.1. Materials

A PGMs mine sludge sample contaminated with hydrocarbons was sourced from one of the UG2 ore processing plants in the Limpopo province, South Africa. The non-ionic surfactant Triston 10 (TX-100), chemically known as Polyethylene Glycol Octyl Phenyl Ether, was supplied by Merck, South Africa. H_2SO4 and NaOH, which were used as pH regulators, were also supplied by Merck, South Africa. All reagents were of analytical research (AR) grade.

2.2. Mineralogical and surface morphology characterization of the hydrocarbon contaminated PGM mine sludge

To determine the chemical composition of the PGMs mine sludge sample, Rigaku ZSX Primus X-ray fluorescence (XRF) equipment was used. To determine the mineral composition of the PGM mine sludge sample, Rigaku Ultima V X-ray diffraction (XRD) equipment was used, where X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons by applying a voltage of 20 to 45 Kv and bombarding the CuK_α radiation target material with electrons. To show how liberated the particles are in the PGMs mine sludge, TESCAN Vega 3XMU scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) equipment was used. The sample was degreased prior to being put on top of the mould to increase adherence during the preparation for the scanning electron microscopy analysis. To determine the presence of hydrocarbon functional groups present in the PGM mine sludge sample, Fourier transform infrared spectroscopy (FTIR) equipment was used.

2.3. Mine sludge washing experiments

1kg of the PGM mine sludge was used for each experimental run. Firstly, 5L of H_2O was poured into a 10L bucket and the pH was then adjusted according to the design of experiment table (Table 1) using the pH regulators and conditioned for 5 minutes. After conditioning, a measured amount of the surfactant was added into the 5L bucket and pH adjusted once again while conditioning the mixture for another 5 minutes. After the conditioning time, 1kg of the sample was then poured into the conditioned pulp and Triston-100 (TX-100) surfactant was also added. Washing time was then measured according to (RSM-BBD) design of experiments. After washing, the remaining solid sample was separated from the solution using filtration process. The resulting sample was then taken for FTIR analysis to determine the presence of hydrocarbons in the sample after washing. After the FTIR analysis, the formula (1) below was used to calculate the hydrocarbon percent removal (%R) of hydrocarbons:

$$\%\boldsymbol{R} = \frac{\boldsymbol{C_o - C}}{\boldsymbol{C_o}} \times \mathbf{100} \tag{1}$$

Where C_o and C were the contaminant concentrations before and after washing detected in the washed sample, respectively.

2.4. Design of washing experiments

For the design of washing experiments, the (RSM-BBD)was used to optimize the remediation of the hydrocarbons from the PGM mine sludge [6]. The factors investigated were the pH of the slurry, concentration of the surfactant and the washing time. 15 experiments were conducted as shown in Table 1.

Table 1: The designed experiments using Box Behnken Design.

Experiment No.	Washing Time (min)	pH	Triston-100 (TX-100) Surfactant Concentration (g/kg)
B1	150	12	15
B2	90	8	15
B3	30	8	25
B4	90	12	25
B5	30	12	15
B6	150	4	15
B7	90	8	15
B8	90	4	5
B9	90	12	5
B10	90	8	15
B11	90	4	25
B12	150	8	25
B13	30	8	5
B14	150	8	5
B15	30	4	15

3. Results and Discussion

3.1. Chemical Composition of the PGM mine sludge

To determine the chemical composition of the PGMs mine sludge sample as received, the XRF was used and the results are represented in Table 2. Based on Table 2, the PGMs mine sludge contained mainly 24.77% of iron, followed by 12.12% of silicon and lastly 8.43% of chromium. The mine sludge contained base metals such as Fe, Ni, Cu, Co and Zn which indicates that sulphides can be found in the sample. The presence of chromium in the mine sludge sample might also indicate the presence of chromium spinels in the sample. The sample did not have any toxic elements in it that might make it radioactive, so it safe to handle the sample. The elemental composition of the mine sludge proved that it originated from UG2 ore.

Table 2: XRF results of the as- received sample of the PGMs mine sludge.

Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**	
Element % Wt	0.12	4.03	4.27	12.12	0.03	0.27	0.32	0.34	5.51	0.51	
Element	**V**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**Sr**	**Zr**	**Co**	**O**
Element % Wt	0.13	8.43	0.21	24.77	0.41	0.08	0.14	0.03	0.01	0.03	38.24

The sample was analysed for (Pt, Pd, Rh and Au) using nickel sulphide fire assaying and the results revealed that the sample contained 5.68, 2.95, 0.6 and 0.09g/t respectively, giving a total of 9.32g/t. This indicates that the sample is of very high grade and it is worthy processing it.

3.2. Mineralogical Phases of the PGMs mine sludge

The phases present in the PGMs mine sludge were determined using the XRD (Fig. 1). It shows that the samples contain sulphides like sphalerite, covellite, chalcopyrite and cubanite. Quartz and chromite were also detected as some of the main gangue minerals present in the sample. These results may partially confirm that this sample is of UG-2 origin. Generally, PGMs are associated with base metal sulphide minerals, chromite and silicate matrices in UG-2 ore.

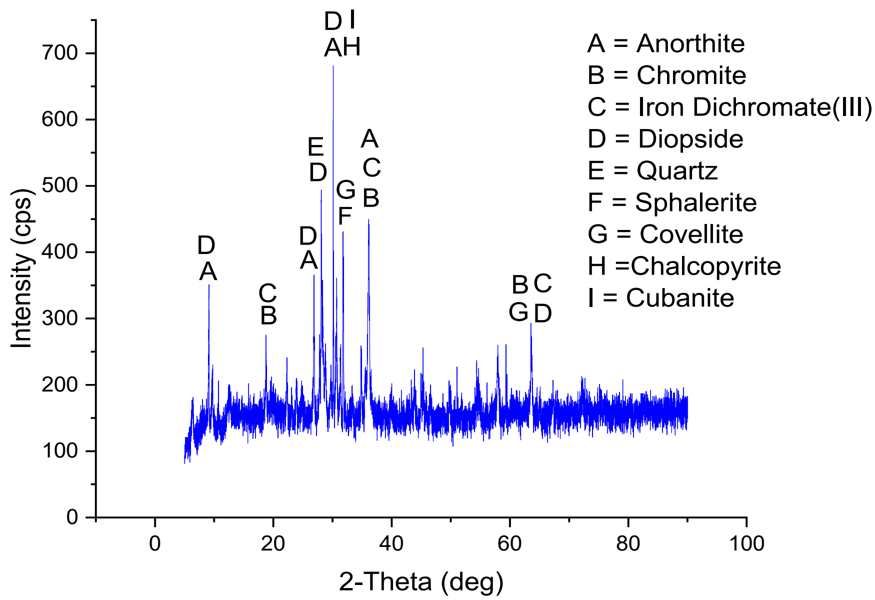

Fig.1: XRD spectra of the PGMs mine sludge.

3.3. Surface Morphology of the PGMs mine sludge sample

The surface morphology of the PGMs mine sludge was determined using the SEM-EDX equipment as shown in Fig. 2 and Table 3, respectively. The results show that the sample contains minerals like chromite, chalcopyrite, covellite, anorthite and cubanite. These results agree with the XRD spectra (Fig. 1) in terms of the minerals present in the sample. The content of the SEM-EDX analysis differs from that of the XRF because the SEM-EDX analysis only focuses on one spot as compared to XRF that focuses on the entire sample being analysed. Fig. 2(A and B) show the major phases that contain the valuable and the gangue minerals. Figure 2B shows that the PGMs are found in mineral phases of diameter 5.98 µm. The most probable phases found at spectrum 1 (Fig 2C) are: chromite, anorthite, cubanite, chalcopyrite and PGMs sulphide minerals whilst those found at spectrum 2 (Fig 2D) are: Chromite, anorthite, covellite and chalcopyrite. This shows that PGMs are found associated with base metal sulphides as well as within chromite matrix. The Fig. 2C show the presence of platinum (Pt), palladium (Pd) and iridium (Ir) at a concentration of 0.16, 0.02 and 0.27% respectively. This confirms the presence of PGMs in the sample. The phase containing PGMs is well liberated and there is no need to mill the sample further. However, the phase is very fine and this will give challenges in the flotation stage.

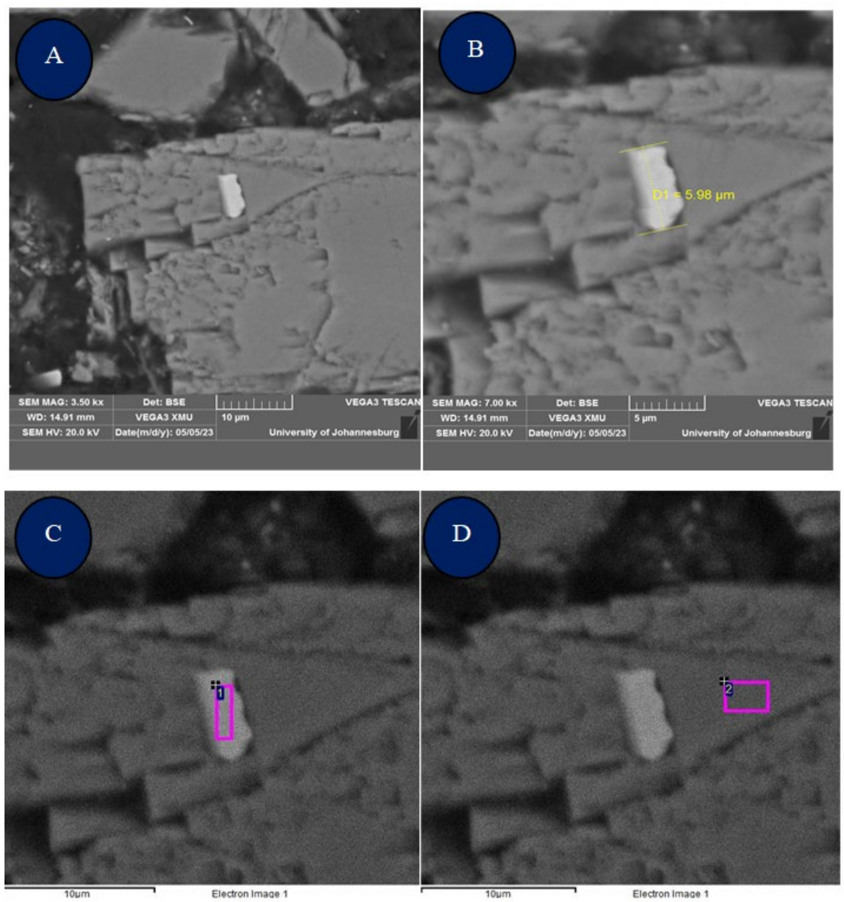

Fig. 2: SEM-EDS images of the PGMs mine sludge

Table 3: Chemical composition of the PGMs mine sludge (EDS).

Elements	**O**	**Cr**	**Ag**	**Mg**	**Al**	**Si**	**Pd**	**Os**	**Ir**
Spectrum 1	46.20	0.31	0.16	16.66	0.34	28.67	0.02	0.51	0.27
Spectrum 2	41.95	10.09	-	11.98	4.66	18.91	-	-	
Elements	**Pt**	**Ca**	**Ti**	**V**	**Fe**	**Mn**	**Cu**		
Spectrum 1	0.16	0.31	-	-	6.19	0.20	0.13		

Spectrum 2	-	0.17	0.16	0.18	11.90	-	0.04

3.4. Functional groups present in the PGM mine sludge sample

To determine the presence of hydrocarbons in the PGMs mine sludge, FTIR was used and the results are shown on Fig. 3. The FTIR method used to characterise the solid sample was the KBr method which introduced alcohols (O-H bonds) in the sample and its peaks are from the range of 3000-3700cm^{-1} [7]. The general range of the wavenumber of hydrocarbons (C-H bond) is 2850-3000cm^{-1}. As shown on Fig. 3, hydrocarbons (C-H bond) are present in the PGMs mine sludge sample. Therefore, this confirms that the PGMs mine sludge sample is contaminated with hydrocarbons.

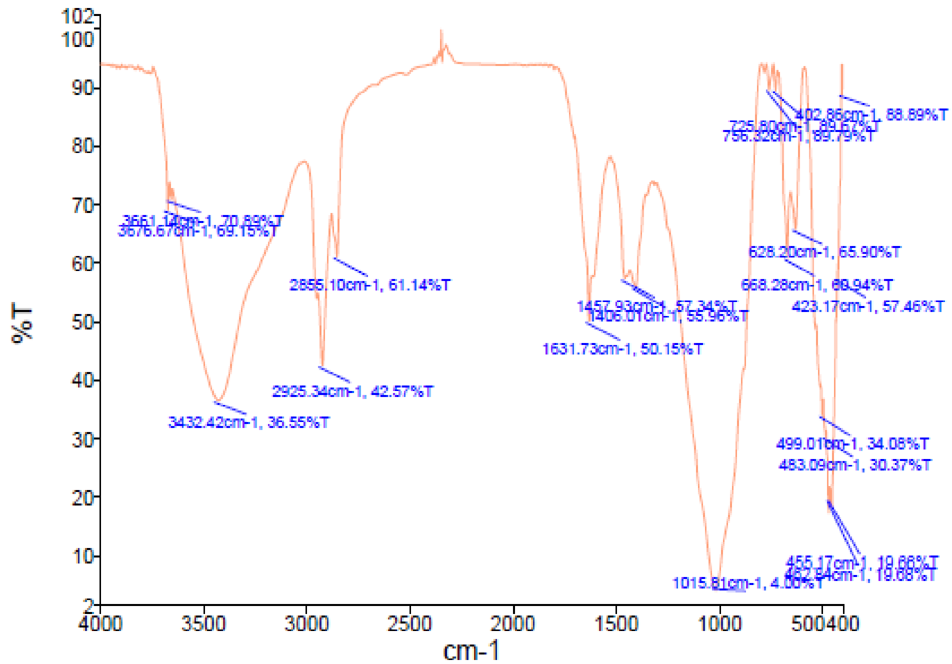

Fig. 3: FTIR results of the PGM mine sludge.

3.5. Washing experiment results

The efficiency of the washing experiments was calculated following equation 1 and the results are shown in Table 4. The average hydrocarbon concentration (C_o) in the as-received sample of the PGMs mines sludge was found to be 58.3ppm. B1 showed the highest hydrocarbon removal efficiency with 91.86%, followed by B4, with 79.87 %. The lowest hydrocarbon removal efficiency was achieved at B10, with 50.20%.

Table 4: Concentrations of the hydrocarbons in PGM mine sludge after washing experiments and the calculated hydrocarbon removal percent in the sample.

Experiment No.	Hydrocarbon concentration after washing (ppm)	Hydrocarbon removal (%)
B1	4.75	91.86
B2	22.67	61.12
B3	24.91	57.28
B4	11.74	79.87
B5	13,.05	77.63

B6	16.17	72.28
B7	24.89	57.32
B8	12.91	77.87
B9	27.60	52.68
B10	29.04	50.20
B11	12.72	78.20
B12	24.43	58.11
B13	22.63	61.19
B14	28.86	50.51
B15	15.70	73.08

4. Conclusion

Hydrocarbon contaminated PGMs mine sludge has great potential as a source of PGMs. The mine sludge contains a high grade of PGEs. Most of the PGM are associated with base metals, chromite and silica. The FTIR results have shown that the hydrocarbons were presents in the sample at the wavenumber of is 2850-3000cm^{-1} of the sample. The SEM-EDX results revealed that the sample is fully liberated and no further milling is required. However, the grain sizes are too fine (D- 5.98) and they will be difficult to process using froth flotation. An optimum hydrocarbon removal of 91.86% was achieved under optimum washing conditions of a pH of 12, Triston- 100 (TX-100) dosage of 15g/kg and washing time of 150 minutes. Further studies on the application of other non-ionic surfactants and the flotation behaviour of the washed mine sludge are recommended.

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