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Characterization of Hydrocarbons Contaminated Platinum Group Metals Mine Sludge from the Bushveld Complex

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***Abstract* -** Mechanized mining methods adopted in platinum-group elements (PGE) industry leads to mobile machinery leakages which result in mine sludge contamination by hydrocarbons. This paper aims at investigating the mineralogical characteristics of the contaminated mine sludge in comparison to the pristine ore. Two types of samples were used in the study were pristine PGE ore and contaminated PGE mine sludge. The samples were analysed using FTIR, XRF, XRD, SEM-EDS, Fire assaying, ICP-OES and Malvern PSD analyser for elemental composition, mineral composition, particle size distribution and the presence of hydrocarbon functional groups. FTIR results indicated the presence of a single C-H bonds in the contaminated mine sludge, which is the hydrocarbons functional group and pristine PGE ore was found to be free from an indication of such contaminants. The fire assaying results revealed that the mine sludge contained a total of 9.32g/t 4E (5.68 ppm Pt, 2.95ppm Pd, 0.6ppm Rh and 0.09ppm Au) and the pristine ore 4.74g/t 4E (2.64ppm Pt, 1.63ppm Pd, 0.42ppm Rh and 0.05ppm Au). SEM-EDS further confirmed that the sludge is indeed richer in PGE than pristine PGE ore. Mineral phases identified by XRD included millerite, chalcocite, aluminium oxide, chalcopyrite, pyrite, pyrrhotite, pentlandite, anorthite, enstatite and magnesium chromite and they were common to both samples. Particle size analysis revealed that the hydrocarbon contaminated mine sludge and the pristine ore had a P80 of 169 and 252µm respectively. Both samples had approximately 4% of fines (<10 µm). Remedial of hydrocarbon contaminants would lead to high grade PGE recovery.

***Keywords*:** Platinum-group elements, mechanized mining, flotation, mine sludge, hydrocarbons, Bushveld complex.

1. Introduction

Mechanized mining is widely practised as a mining method particularly in newer mines in South Africa. The operation involves the use of "off track" or trackless machinery. Diesel is the most widely used fuel for such machinery in industrial sectors such as transportation, mining, and construction due to the much-needed high-power output it provides [1]. Due to the heavy nature of such machinery, piping failure may lead to oil spillage, resulting in contamination of the mine sludge [2]. The platiniferous deposits of the Bushveld Igneous Complex (BIC) have been mined for a long time and in the process mine sludge has been produced. It has been piled up and there is need to recover PGMs locked in it [3].

Platinum-group minerals (PGMs) are recovered by bulk sulphide froth flotation process using sodium isobutyl xanthate as the main collector. Flotation efficiency increases with the degree of ore minerals liberation. However, finer ore minerals may result in slimes formation, with PGEs entrained in the slimes. The latter result into low recovery of PGMs during flotation process [4]. Flotation of hydrocarbons contaminated ore for the removal of such contaminants involves the use of surfactants, which introduces challenges when it comes to rinsing of the ore after the process [5]. This poses a challenge as new flotation conditions need to be established for the recovery of PGEs after removal of such contaminants. This paper focusses on characterization of hydrocarbons contaminated mine sludge in comparison with pristine PGE ore, with the aim of recovering PGE from such contaminated mine sludge.

2. Methodology

2.1. Materials

The samples used in all the experimental procedures and analysis were obtained from one of the PGMs processing plant in Mpumalanga Province, South Africa. The samples were first homogenized using rotary sample splitter, relevant samples were then taken as per methodology requirements for the relevant experiment or analysis. Two categories of samples were taken from two separate mining stockpiles. The first sample (Sample (I)) was the hydrocarbons contaminated mine sludge and the second sample (Sample (II)) was the pristine PGE ore. Sampling was done in such a way that it best represented the bulk material.

2.2. Methods

The two samples were pulverized to < 75µm and analysed to determine the presence of hydrocarbons functional groups using Nicolet Is10 Fourier transform infrared spectroscopy (FTIR). The chemical composition of the two samples was done using RigakuZSX Primus II XRF analysis equipment. Sample preparation involved pulverizing each sample to -75µm, mixing 10g of the sample with 5g of Sasol wax binder, then pelletizing using pelletizer equipment and analysed. To determine the 4E (Pt, Pd, Rh, Au) grade, fire assaying using a nickel sulphide collector was used followed by inductively coupled plasma - optical emission spectrometry (ICP-OES) analyses. The mineralogical phases identification was done using RigakuUltimaIV XRD analysis equipment. Sample preparation involved pulverizing each sample to -75µm. The sample was then analysed in its powder form. The surface morphology analysis was done using TESCAN Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Sample preparation involved first mounting 10g of each sample with 15ml epoxy resin and 2ml epoxy hardener, then polishing the mounts prior to analysing.

3. Results and discussions

3.1 Functional group results

The mine sludge and pristine ore were analysed with FTIR equipment to determine the functional groups and the results are shown in Fig. 1. Pristine ore showed absence of peaks in the diagnostic region (>1500cm^{-1}), thus, the ore has no indication of hydrocarbon contaminants. Contaminated mine sludge results show occurrence of a peak in the diagnostic region at approximately 2920cm^{-1} wavelength. The transmittance table for FTIR results interpretation shows that the wavelength 2920cm^{-1} indicates the presence of C-H bond in the sample, which is the functional group for hydrocarbons. It can, therefore, be partially concluded that the PGE mine sludge has hydrocarbon contaminants.

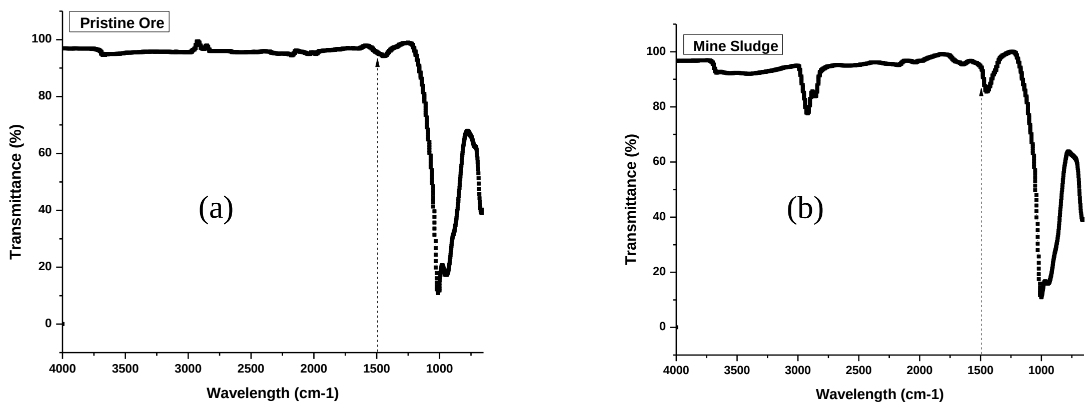

Fig. 1: FTIR spectra of (a) Pristine PGE ore and (b) Contaminated mine sludge.

3.2 Chemical composition results

The chemical composition of the two samples was determined using XRF and the results are shown in Table 1. According to Table 1, the dominant elements were Si, Fe, Mg, Cr, Ca, and Al differing in amounts. Other trace elements of ≤1% were detected.

Table 1: Elemental composition of pristine ore in comparison with hydrocarbons contaminated mine sludge.

Element	Si	Fe	Mg	Cr	Ca	Al	Ti	Na	K	Ni	Mn
Pristine ore (%Wt.)	30.3	21.78	15.89	13.69	7.51	8.46	0.72	0.48	0.35	0.26	0.24
Mine sludge (%Wt.)	24.3	8.2	9.89	17.09	9.2	7.53	1.08	0.24	0.46	0.43	0.27
Element	S	V	Co	Zn	Cu	P	Cl	Sr	Pb	Rb	Cl
Pristine ore (%Wt.)	0.18	0.16	0.03	0.04	0.04	0.03	0.05	0.03	0	0	0.05
Mine sludge (%Wt.)	0.56	0.18	0.04	0.19	0.13	0.09	0.05	0.07	0.03	0.02	0.05

The presence of silica indicates an abundance of gangue material. Fe, Mg, and Al in combination with S found in both samples indicate the possibility of base metal sulphides pyrrhotite and pyrite and naturally floating magnesium silicate gangue. Nickel may be an indication of millerite and pentlandite in the sample, even though it occurs as one of the trace elements in the samples. The Cr indicates the existence of chromite spinel in the form of either $FeCr_2O_4$ or $MgCr_2O_4$. It can therefore be partially concluded that the ore is of UG2 origin, based on the indication of chromite silica-based gangue minerals and base-metal sulphides [7]. PGEs were not identified as these are below the detection limit. The instrument cannot accurately detect elements with $Z<11$ in most natural earth materials.

3.3 4E grade of the fresh ore and contaminated mine sludge

Table 2 represents 4E fire assay results comparison of pristine PGE ore and contaminated mine sludge. The ICP-OES results showed that the contaminated mine sludge is richer in all four elements than pristine ore. There is also a decreasing concentration trend of both samples for all four elements, with Pt being the most concentrated, followed by Pd, Rh then a minute amount of gold [7].

Table 2: 4E fire assay results comparison of pristine ore and contaminated mine sludge

Element	**Pristine ore(ppm)**	**Contaminated mine sludge(ppm)**
Pt	2.64	5.68
Pd	1.63	2.95
Rh	0.42	0.6
Au	0.05	0.09
Total	**4.74**	**9.32**

This shows that the hydrocarbons contaminated mine sludge is of higher grade as compared to pristine PGE ore and the sludge is almost two folds higher in grade than pristine PGE ore.

3.4 Mineral phases results

Fig. 2 represents a comparison of pristine PGE ore and hydrocarbons contaminated mine sludge XRD spectra. Both samples showed mineral phases identified as millerite, chalcocite, aluminium oxide, chalcopyrite, pyrite, pyrrhotite, pentlandite, anorthite, enstatite and magnesium chromite. This agrees with XRF results with dominant elements Si, Fe, Mg, Cr, Ca, and Al. The dominant phases are anorthite gangue and magnesium chromite spinel from both samples. The presence of naturally floating pyroxenes such as enstatite an anorthite were also detected from both samples.

The XRD patterns appear to be the same for the samples, although the mineral phases in the pristine PGE ore sample occur with more intensity than those of the hydrocarbons contaminated mine sludge. The low intensity of mineral phases of the hydrocarbons contaminated PGE sludge is because its mineral phases occur as amorphous because of the presence of hydrocarbon contaminants that supress the mine sludge structure.

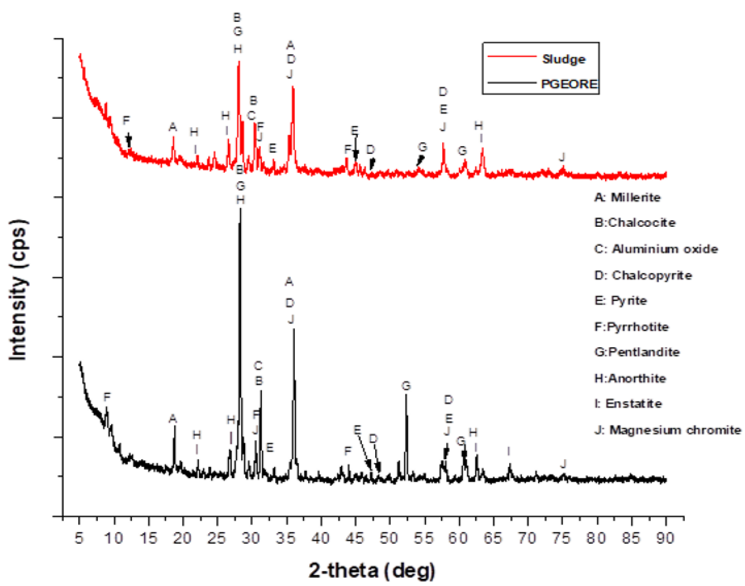

Fig. 2: Comparison of XRD spectra of pristine PGE ore and hydrocarbons contaminated mine sludge.

The pristine PGE ore mineral phases occur in crystalline form, hence, the high intensity of such phases. Based on the mineral phases detected above, a partial conclusion can be drawn that both the ore and the sludge are of UG2 origin [7].

3.5 Surface Morphology of the pristine ore and mine sludge samples

The surface morphology of the samples was determined using SEM-EDS and the results are shown in Fig. 3 and Tables 3 and 4. The SEM micrograph results show that both samples mineral grains are partially liberated. The results also showed that the mineral phases dominant in both pristine ore and the hydrocarbons contaminated mine sludge are the naturally floating pyroxene minerals: anorthite, enstatite, together with chromite. The high amounts of silica (ore-23.43% maximum, sludge-23.44% maximum) further suggests that the samples are of chromite and silica-based gangue. This agrees with the XRD results. Chromite content is not in agreement with XRF results, where the case is vice versa. This is due to the analysis method that XRF analyses the sample on average, while SEM chooses a spot to analyse.

(a) (b)

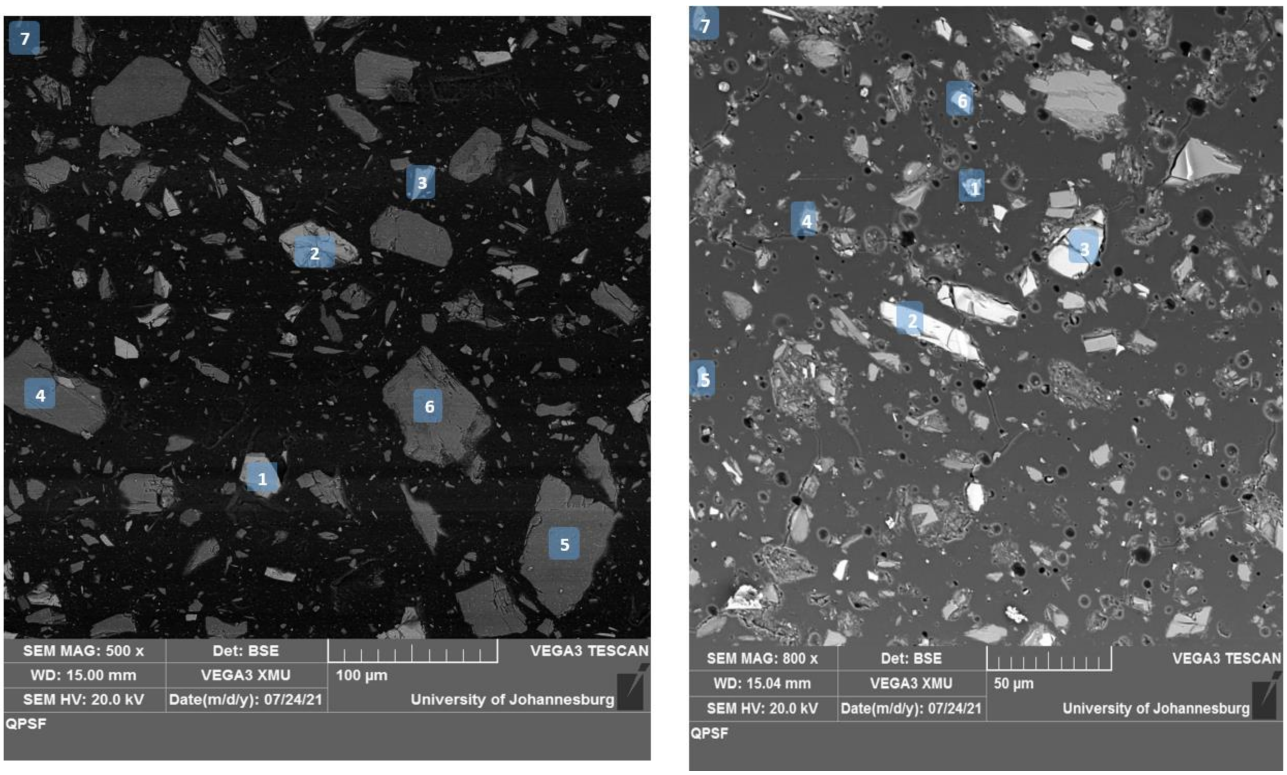

Fig 3. Morphology results of (a). Pristine ore and (b). Mine sludge

The results further indicated that pristine ore showed a maximum of 0.04% Pt, while the sludge showed a maximum of 0.18% with 0.1%Pd. This indicates that the contaminated sludge is of high PGE grade than the pristine ore. XRF results also agree. A partial conclusion can be drawn that both the pristine ore and the contaminated mine sludge are of UG2 origin, given the chromite-silica-based gangue, and the presence of base metal sulphides such as pyrite, chalcopyrite, pyrrhotite etc. The presence of pentlandite in the mine sludge further partially concludes that the sludge in indeed richer in PGEs than the pristine ore as majority PGEs occur in pentlandite as compared to other base metals at the Bushveld complex [7].

Table 3: Chemical composition of pristine ore spectra

Spectrum no.	Elements (Wt. %)												Possible phases
	O	Mg	Al	Si	S	K	Ca	Cr	Fe	Pt	Na	Cu	
1	72.12	6.42	2.19	10.08	1.00	0	0.71	1.81	1.96	0	0	0	Chromite, anorthite, enstatite, pyrrhotite, pyrite
2	51.84	0.96	15.17	22.69	0	0	6.41	0	0.41	0	5.51	0	Anorthite, enstatite
3	75.10	4.83	1.49	9.41	0	0	1.47	0.80	1.16	0	0	0	Chromite, anorthite, enstatite,
4	52.70	12.90	1.95	23.30	0	0	4.38	1.12	2.22	0	0	0	Chromite, anorthite, enstatite,
5	50.82	1.45	14.80	23.43	0	0	6.45	0.19	0.60	0	1.76	0	Chromite, anorthite, enstatite,
6	55.10	11.83	5.01	19.51	0.15	1.13	2.0	1.12	3.12	0.02	0	0	Chromite, anorthite, enstatite, pyrrhotite, pyrite, platinum
7	57.60	8.56	7.16	17.74	0.22	0	2.46	2.0	2.50	0.04	0.96	0.05	Chromite, anorthite, enstatite, pyrrhotite, pyrite, chalcopyrite, platinum

Table 4: Chemical composition of mine sludge spectra

Spectrum no.	Elements (Wt. %)													Possible phases
	O	Mg	Al	Si	S	Ca	Cr	Fe	Pt	Pd	Ni	Cu	Na	
1	70.93	2.01	3.57	13.41	1.00	0.42	0	0	0	0	0	0	1.63	Anorthite, enstatite, pyrrhotite, pyrite,
2	73.21	7.69	8.63	5.60	0	0	1.61	0.69	0	0	2.58	0	0	Enstatite, Anorthite
3	76.70	5.87	5.61	7.17	0.63	0.38	0	0	0	0	2.66	0	0	Anorthite, enstatite, pyrrhotite, pyrite, pentlandite
4	62.36	9.76	3.22	14.36	0.59	0.62	0	0.59	0	0	6.65	0	1.09	Anorthite, enstatite, pyrrhotite, pyrite, pentlandite
5	62.35	11.41	4.88	17.62	0.55	0.73	0.72	0.87	0.06	0	0.38	0	0	Chromite, anorthite, enstatite, pyrrhotite, pyrite, pentlandite, platinum
6	57.41	16.34	0.65	23.44	0	0.20	0	1.43	0.15	0.10	0.22	0	0	Anorthite, enstatite, pyrrhotite, pyrite, pentlandite, platinum, palladium
7	69.37	7.60	4.22	11.99	0.67	0.84	0.53	0.71	0.18	0	2,45	0.01	0.49	Chromite, anorthite, enstatite, pyrrhotite, pyrite, chalcopyrite, platinum

3.6 Particle size distribution of the fresh and contaminated mine sludge

Fig. 4 represents PSD results of pristine ore in comparison with hydrocarbon contaminated PGE mine sludge. The results showed that pristine ore has 80% passing 252µm size fraction, while the contaminated sludge has 80% passing 169µm. This shows that the contaminated mine sludge is finer than pristine ore. The PGMs are finer and will therefore most likely be on the finer fractions (i.e., the sludge).

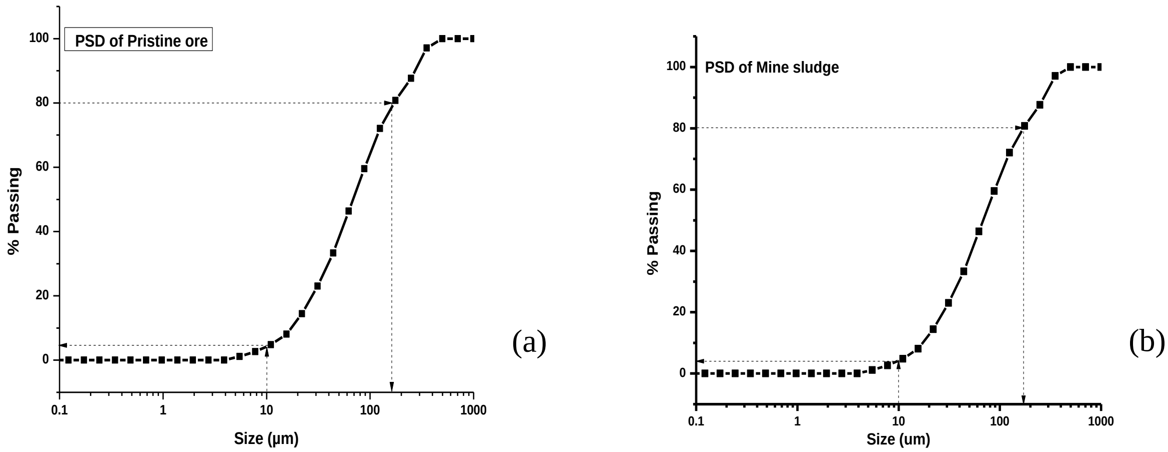

Fig.4: PSD results of (a) pristine PGE ore and (b) hydrocarbon contaminated mine sludge

4. Conclusion

The objective of this work was to characterise a hydrocarbons contaminated PGE mine sludge with the aim of recovering PGMs by flotation process. From the results, it was found that the mine sludge is contaminated with hydrocarbons, whilst pristine PGE ore is free from such contaminants. XRD and SEM-EDS results showed that both samples are dominated with silica-based and chromite gangue, both having the same base-metal sulphides occurrence in them, which concludes that the ore and the contaminated sludge are of UG2 origin. XRD results further showed that the mine sludge has more pentlandite than pristine PGE ore and fire assaying proved that it has higher PGE grades. From the particle size analysis results, it can be concluded that fines are not another factor adding to challenges in processing the ore and the sludge for recovery in the plant, only 4% fines for both. It is therefore proposed that the removal of hydrocarbon contaminants be carried out before flotation as the sludge is of even better grade than the pristine ore.

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References

[1] G. Geldenhuys, E. R. Rohwer, Y. Naude' and P. B. Forbes, ‘‘ Monitoring of atmospheric gaseous and particulate polycyclic aromatic hydrocarbons in South African platinum mines utilising portable denuder sampling with analysis by thermal desorption–comprehensive gas chromatography–mass spectrometry,” *J. Chromatogr*, vol. 1380, pp.17-28, 2015 .

[2] J. Steyn, ‘‘Hydrocarbons's number one adversary: risk management ’’ *Inside Mining*., vol. 3, no. 3, pp. 3-5, 2010.

[3] W. Nheta and K. Mapotsane, K., 2017. ‘‘Recovery of pgms from mine sludge by leaching*, ’’* in *17th International multidisciplinary scientific geoconference sgem,*Varna, Bulgaria, 2017, pp. 987-994.

[4] N.A. Chapman, N.J. Shackleton, V. Malysiak and C.T. O’Connor ‘‘The effect of using different comminution procedures on the flotation of Platinum-Group Minerals’’. *Miner. Eng.,* vol 24, no. 8, pp. 731-736, 2011.

[5] J. Mouton, J, G. Mercier and J. F. Blais, ‘‘Laboratory-scale flotation process for treatment of soils contaminated with both PAH and lead, ’’ *J. Environ. Eng,* vol. 136, no. 10, pp. 1063-1074. 2010.

[6] R. Cawthorn, ‘‘The platinum group element deposits of the Bushveld Complex in South Africa, ’’ *Platin. Met. Rev.*, vol 54, no. 4, pp. 205 - 215. 2010.

[7] F. Crundwell, M. Moats, V. Ramachandran, T. Robinson and W,G. Davenport. *Extractive metallurgy of nickel, cobalt and platinum group metals*, ’’ Elsevier, 2011.