Removal of Hydrocarbon Contaminants from a PGM Mine Sludge using an Anionic Surfactant

T. C. Govindsamy and W. Nheta

Abstract—Mechanised mining in the Platinum Group Metal industry has led to hydrocarbon-fuel leaks from mobile machinery, which result in the formation of contaminated mine sludge. The formed mine sludge contains high-grade PGMs, and it is imperative to process it. However, conventional flotation circuits produce very low recoveries, leading to the piling of this valuable resource. PGM-contaminated mine sludge washing experiments were conducted using an anionic surfactant to investigate the removal of hydrocarbons prior to the flotation process. Particular attention was paid to the effect of the surfactant on hydrocarbon removal by evaluating the washing parameters such as surfactant concentration, washing time and liquid-solid ratio. The characterisation of the PGM mine sludge was done using a fire assay and showed a significant value of 9.32ppm of 4E PGE’s (Pt, Pd, Rd and Au), and hydrocarbon determination done by FTIR analysis showed the presence of hydrocarbon functional groups in the mine sludge. The use of RSM as an optimising tool was applied to the washing experiments. The washing results showed the highest hydrocarbon removal of 94.75% by using the anionic surfactant sodium dodecyl benzene sulfonate (SDBS) at a concentration of 2.5%, a washing time of 120 minutes at a solid-liquid ratio of 1:10. The hydrocarbon removal increased with an increase in the concentration of the surfactant. It was observed that the desorption of the hydrocarbons increased as the washing time increased. However, the presence of clay minerals in the PGM mine sludge was disadvantageous to the removal of hydrocarbons, as hydrocarbons tend to bind and sorb to small particles.

Keywords— PGMs, Flotation, Mine sludge, Hydrocarbon contaminants, Surfactants.

I. Introduction

Since the incline in demand for Platinum Group elements (PGE) such as platinum, palladium, rhodium, ruthenium, iridium and osmium is ongoing, there is still a need to investigate beneficiation processes and improve recovery of Platinum group elements [1]. Located in the north of South Africa, the Bushveld igneous complex (BIC) is home to the PGM-ore bearing deposits which comprises the Upper Group 2, Merensky Reef and Plat Reef. They run across the eastern, western, and northern limbs of the BIC [2]

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South Africa contributes to about 90% of the world's reserves in PGMs and is significantly used in various industrial applications such as the hydrogen economy, catalysts, batteries, medical applications and so many more, therefore the need to enhance better exploitation of these abundant precious metal reserves are pertinent to study [3]. The Platinum group mining operations occur at open cast and underground levels which require drilling and blasting methods to mine valuable PGM ore [4].

The advancement in mining technologies has led to the mechanisation of trackless mobile machinery which operates at deeper levels underground and is currently powered by hydrocarbon-based fuels. Hydrocarbon fuels in the form of diesel oil and crude oil may leak from the heavy-duty machinery which are used in mining and transportation of the ore [5]. Subsequently, after the blasting process, the fuel spillage from the machinery, along with water from dust sprays combine to form a mine sludge which is piled up and stored. The presence of contaminants in the mine sludge reduces the capabilities of the froth flotation technique and results in the lower recovery of PGMs if not removed [5].

The use of surfactants in the removal of hydrocarbon contaminants during the washing process results in successful removal however displays some challenges to the flotation process. The current investigation focused on the influence of the washing time, surfactant concentration and solid-liquid ratio on the removal of hydrocarbon contaminants using an anionic surfactant. Its effectiveness was explored using the Response Surface Methodology approach.

II. Methodology

A. Materials

A hydrocarbon-contaminated PGM mine sludge was obtained from a PGM ore processing plant in the Limpopo Province, in South Africa. The anionic surfactant Sodium dodecyl benzene sulfonate (SDBS) of analytical research grade was supplied by Merck, South Africa.

B. Final Mineralogical and surface Characterization of the hydrocarbon-contaminated PGM mine sludge

The chemical composition of contaminated PGM mine sludge was done using the RigakuZSX Primus II X-ray fluorescence (XRF) analysis. The PGM content was obtained using fire assaying followed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The Rigaku Ultima

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V X-Ray Diffraction (XRD) equipment was used to determine the mineral composition of the PGM mine sludge. To determine the presence of hydrocarbon functional groups, present in the PGM mine sludge sample, Fourier transformation infrared spectroscopy equipment was used. The Tescan Vega 3Xmu scanning electron microscopy (SEM) was used to display the extent of the liberation of the particles in the PGM mine sludge.

C. Design of the PGM mine sludge washing experiments

The PGMs mine sludge washing experiments were designed using RSM. A series of experiments were done to investigate the effect of washing parameters such as surfactant concentration, washing time and liquid-solid ratio according to the conditions presented in Table I.

TABLE I: THE DESIGN OF THE PGMS MINE SLUDGE WASHING EXPERIMENTS

Batch number	Time (Min)	Reagent Concentration (%)	Solid-Liquid Ratio
1	30	2.5	10
2	75	1.75	20
3	30	1	30
4	120	2.5	30
5	120	1	10
6	75	3.0	20
7	150.7	1.75	20
8	30	1.75	20
9	75	0.49	20
10	120	1	30
11	30	1	10
12	75	1.75	3.18
13	75	1.75	36.8
14	30	2.5	30
15	120	2.5	10

D. Washing Experiments

The washing experiments were done by varying the surfactant concentration, washing time and solid-liquid ratio. Each experimental run comprised a varying parameter which was conducted according to the design of the experimental table (Table I) and filled up to a volume of 500ml in each run. For each run, a specific amount of surfactant was added to prepare a desired concentration as per the table and stirred until all surfactant particles were dissolved and thereafter a known dried mass of the hydrocarbon-contaminated mine sludge was added. The surfactant-mine sludge mixture was agitated at 1000rpm in a cell for set time intervals for washing. Thereafter the washed sample was separated into both solids and solution by the filtration process. The sample was then dried in the oven to remove excess moisture and later analysed for hydrocarbon contamination. The hydrocarbon quantification was done by mixing 300ml of acetone with 50g of dried sample taken from the washing experiment. The mixture was then stirred with a magnetic stirrer on a metal plate for 1 hour and the solids left to settle and separate into solids and liquid. The liquid then underwent the distillation process whereby the temperature was set at 80 degrees Celsius which allowed for the evaporation and condensation of the acetone. The hydrocarbon residue was left in the cylindrical beaker after the distillation process. The hydrocarbon oil residue was poured into glass crucibles that were weighed initially and when containing the hydrocarbon residue to determine the mass of the hydrocarbon contaminants. % hydrocarbon removal was then calculated using the following equation.

$$\%R = (Ci - Cf)/Ci \times 100 \quad (1)$$

Where Ci and Cf were the hydrocarbon contaminant concentrations before and after the washing experiment respectively.

III. RESULTS AND DISCUSSION

A. Elemental and chemical composition of the PGM mine sludge

The chemical composition of the PGM mine sludge was determined using XRF, and the results are represented in Table II. The PGM mine sludge comprised mainly 24.68, 11.66 and 8.54% of Fe, Si and Cr respectively. The PGM mine sludge also displayed base metals sulphides such as Ni, Cu, Fe and Zn, but minor concentrations. Fire assaying followed by ICP- OES revealed that the mine sludge contained 9.32ppm of 4E PGE's (Pt, Pd, Rd and Au).

TABLE II: THE CHEMICAL COMPOSITION OF THE CONTAMINATED MINE SLUDGE

Element	**Fe**	**Si**	**Cr**	**Cu**	**Ni**	**Zn**
Element % Wt	24.68	11.66	8.54	0.20	0.42	0.16
Element	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**
Element % Wt	0.03	0.18	0.05	0.36	6.51	1.56
Element	**Na**	**Mg**	**Al**	**V**	**Mn**	**Sr**
Element % Wt	0.12	4.15	4.00	0.16	0.20	0.04

B. Mineralogical phases of the PGM mine sludge

The mineral phases present in the PGM mine sludge was detected using the XRD, Fig. 1 below displays the phases present. The sample indicates the occurrence of the main gangue minerals such as silica and chromite, as well as the indication of sulphide minerals such as chalcopyrite and sphalerite. The mineralogical composition is typical of UG2 ore [6].

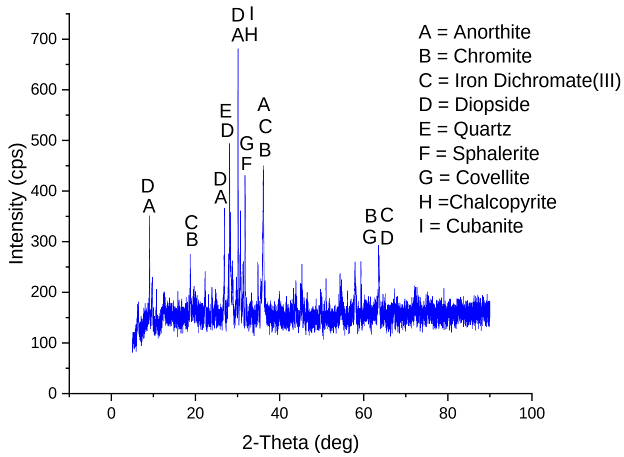

Fig.1. Mineralogical composition of the hydrocarbon-contaminated mine sludge

C. Functional groups present in the PGM mine sludge sample.

FTIR was used to determine the presence of hydrocarbons in the PGM mine sludge sample and the results are displayed in Fig. 2. The FTIR technique used to analyse the PGM mine sludge solid sample by using the KBr method which presented alcohol bonds and displayed peaks that range from 2800-3500cm^{-1}[7]. The general range of the wavenumber of hydrocarbons (C-H bond) is 2850-3000cm^{-1}. This confirms that the mine sludge is indeed contaminated with hydrocarbons.

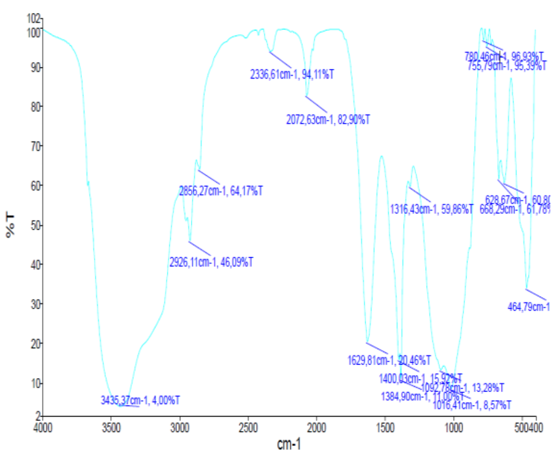

Fig. 2. FTIR of PGM mine sludge sample

D. Washing experiment results

The proficiency of the washing experiments was calculated using Equation 1 and the results are shown in Table III. B15 showed the highest hydrocarbon removal efficiency of 94.75%, trailed by B6 and B4 which displayed efficient removals of 89.14 and 84.88% respectively. B6 proved that an increase in the concentration of surfactant did have a direct increase in hydrocarbon removal. However, it was not as high when compared to B15 with a lower concentration of 2.5% and a longer washing time of 120 minutes that showed the highest removal of hydrocarbons.

TABLE III: HYDROCARBON REMOVAL RESULTS.

Batch number	**Hydrocarbon removal (%)**
1	75.44
2	75.63
3	36.33
4	84.88
5	40.97
6	89.14
7	82.49
8	40.95
9	10.25
10	9.78
11	28.50
12	3.84
13	19.21
14	76.76
15	94.75

IV. CONCLUSION

The study has shed light on the effect of an anionic surfactant (SDBS) washing on the removal of hydrocarbons from a PGM hydrocarbon-contaminated mine sludge. Response Surface Methodology was used to assess the impact of the washing parameters. The PGM-rich contaminated mine sludge has a valuable amount of 9.32ppm of PGES which is of interest to pre-treat. The FTIR analysis indicated that the PGM mine sludge was contaminated with hydrocarbons. The optimum conditions for hydrocarbon removal are a surfactant concentration (SDBS) of 2.5%, a washing time of 120 minutes and a S/L ratio of 1:10. Further research on the flotation behaviour of the washed mine sludge must be conducted to assess the impact of the washing process on the PGM recovery.

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