Sulphidisation of Oxidised PGM Ores to Improve Flotation Kinetics

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ABSTRACT

Research has shown that oxidised Platinum Group Metal (PGM) ores are not amenable to conventional sulphide froth flotation. This is attributed to the oxide layer that is hydrophilic in nature, resulting in poor flotation recoveries and high reagent consumption. As a result, oxidised PGM ores are either left in situ, stockpiled or discarded as waste, presenting a huge resource base that can be exploited given the rapid depletion of pristine (fresh sulphide ores). This necessitates continued research into the processing of oxidised PGM ores. This study was carried out in order to investigate the feasibility of the sulphidisation pre-treatment technique on oxidised PGM ores from a platinum mine in Zimbabwe. The study will contribute to research on alternative techniques that can be employed on oxidised PGM ores. A sample of oxidised ore was obtained from the mine open pit and sulphidised using sodium hydrosulfide (NaHS). Sulphidisation of oxidised ores has been proposed by other researchers as a technique that can enhance flotation kinetics. The addition of a sulphidising agent aims to restore the floatability of the oxidised ores by converting the surface oxides into sulphides. The results of the study showed that sulphidisation of the oxidised PGM ores works efficiently at NaHS dosage of 75 g/t, yielding a recovery of 80% 4E (platinum, palladium, rubidium and gold), whilst unsulphidised ore had a recovery of 40% 4E. This shows the potential of sulphidisation as a viable method to enhance the floatability of oxidised PGM ores.

Keywords: oxidised ore, sulphidisation, PGM, recovery, floatation

Introduction

Platinum Group Metals (PGMs), that is, platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os), play a crucial role in various industrial applications, particularly in catalysis, electronics and jewellery. Their exploitation is due to their unique physical and chemical properties that include excellent catalytic properties, high resistance to corrosion, high melting point and high electrical conductivity, among others (Mudd, 2010).

Conventionally, PGMs concentration was done by flotation from pristine sulphide ores, and this has been successful owing to the occurrence of PGMs in close association with base metal sulphide minerals such as pyrrhotite and pentlandite, which are easy to float. However, the depletion of pristine (unweathered) sulphide PGM ores has prompted the mining industry to explore the processing of oxidised PGMs deposits. These ores are formed due to weathering and oxidation processes, and often present significant challenges in terms of their flotation behaviour and recovery (Sefako, 2018). The oxidation of pristine sulphide PGM ores leads to the formation of oxide layers on the mineral surface, thus rendering them non-floatable using conventional flotation reagents. Equation (1) (Tiisetso & Yongjun, 2022) represents the oxidation process. The equation, however, is too simple to fully explain the mechanism of oxidation of sulphides.

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$$MS + \frac{1}{2}xO_2 + xH_2O \rightarrow M_{1-x}S + xM(OH)_2 \qquad (1)$$

The presence of these oxide layers inhibits the attachment of collector molecules, reduces the hydrophobicity of the mineral surfaces, and compromises the overall flotation kinetics (Sefako *et al*., 2017). The PGMs mine concentrator plants then fail to meet the plant extraction specifications of PGMs when treating oxidised or non-sulphide PGM ores. Consequently, the recovery of valuable PGMs from oxidised ores becomes inefficient and economically unjustifiable.

In recent years, the sulphidisation of oxidised PGM ores has emerged as a promising approach to overcome these challenges and improve flotation kinetics (Newell & Bradshaw, 2007). Sulphidisation involves the addition of a sulphidising agent that reacts with the oxide layers on the mineral surfaces, converting them into sulphides. The process is shown in Equation (2) (Tiisetso & Yongjun, 2022), where M^{2+} and A^{2-} represent the metal cation and the anion in the oxide layer.

$$M^{2+}A^{2-} + 2Na^{+} + S^{-} \rightarrow M^{2+}S^{2-} + 2Na^{+} + A^{2-} \qquad (2)$$

This transformation restores the floatability of the PGM ores and enhances the attachment of collector molecules, thereby improving the overall flotation performance. The process, however, has challenges such as sensitivity to conditioning times, type of sulphidiser and concentration (Tiisetso & Yongjun, 2022; Newell, 2007).

The concentrator at the mine was designed to process sulphide PGM ores, but the established new open pit had 75% of its ore weathered. The flotation results from the tested sections of the pit had exceptionally low PGM recoveries, ranging from 25% to 30% without sulphidisation against the expected recovery of 80% and above. The concentrate grade obtained was less than 10 g/t of Pt and Pd against a target of 40 g/t and above (Sefako, 2018).

Work performed by Zimbabwe Platinum Mines (Zimplats) on flotation of Main Sulphide Zone (MSZ) ores from the Ngezi Mine, as well as work conducted at the Old Wedza Mine and at the Hartley Mine, yielded recoveries of 15% to 30% (Locmelis *et al*., 2010). Attempts made in the South African Bushveld Complex UG2 Reef at Smokey Hills Mine, Impala Platinum Mine in the western Bushveld, and at the Pilanesburg Platinum Mine (PPM) to process PGM ores by flotation also resulted in low and erratic recoveries (typically < 40%) (Becker *et al*., 2014; Oberthür *et al*., 2013). These results illustrated the need to research alternative processing techniques, and sulphidisation is one of the techniques that has proven to be successful in processing oxidised ores. Based on mineralogy studies, oxidised PGM ores proved to have low base metal sulphides (BMS) content, typically about 0.2 wt (Becker *et al*., 2014). Blending the oxidised ore and floating it with pristine ore was tried at Unki Mine, but it resulted in very low

recoveries of 50% (Cramer, 2001). This necessitates further research to identify other processing methods for the commercial exploitation of the oxidised ore.

Flotation remains a promising method for the processing of oxide ores of platinum due to its ability to separate minerals based on their surface properties. Studies conducted so far suggest that sulphidisation of the oxidised ores as a pre-treatment technique can increase recovery of valuable metals, in particular oxidised copper and pentlandite ore (Sefako, 2018). Despite this study, the applicability of the sulphidisation technique on oxidised PGMs ore is yet to be confirmed. The current study, therefore, seeks to confirm the feasibility of the sulphidisation pre-treatment technique on oxidised PGM ores. The results will contribute immensely to research efforts aimed at developing alternative processing techniques for oxidised PGM ores.

Experimental

To determine the feasibility of the sulphidisation pre-treatment method, experiments were carried out on the oxidised ore, sulphidised ore and pristine ore.

Sample Collection

Open pit samples were collected at different depths of the pit using drill bits to obtain a true representation of the sample. Pristine, which is fresh ore from underground, was sampled at the concentrator plant as the primary rougher feed using a sample cutter.

Sample Preparation

The composite sample from the open pit was split into two 20-litre buckets using a 10-way rotary splitter, and subsequently covered with a lid to prevent contamination. The percussion drilling material had initial grinds of 86.15% passing 3.35mm and 28.36% passing 75 microns. Gyrol crushing increased the grind to 98.5% passing 3.35 mm and 28.7% passing 75 microns. Since the grind did not achieve the target of 80% passing 75 microns, it became necessary to mill the material in the rod mill. Prior to rod mill tests, the sample was split into 1 745 g portions to obtain the water solid ratio required in a three-litre float cell of 42% solids. The sample was separately milled at different time intervals to obtain a grinding curve. The pristine sample was filtered and left to air dry, and then lump broken and blended using a rotary splitter.

Fire Assaying

The amount of PGMs in the samples was determined by fire assaying, and a 4E analysis was carried out which are Pt, Pd, Rh and gold (Au). Fire assay is a technique used to determine the metal content of precious metals such as Platinum Group Metals, using high-temperature electric laboratory furnaces. The fire assay process begins by preparing samples in the flux rooms where they are weighed and mixed with a lead flux. The prill obtained after fire assaying was dissolved in aqua regia and analysed using ICP-OES.

Grinding Curve

Grinding was done in a rod mill to obtain the required particle size of 80% passing 75 microns. A sample containing 1 745 g of the ore was placed in the rod mill and 2 455 mls of raw water was added as make up water to produce a pulp of 42% solids. The timer for the rod mill was set at different intervals. The milled sample was decanted from the mill and wet-sieved using a 75-micron screen until a grinding curve was obtained. Seven aliquots were used for estimating the residence time for the sample in the laboratory rod mill to achieve a grind of 80% passing 75 microns.

Flotation Test Work

Float tests were run in triplicate and the concentrates and tails produced were dried for mass pull and assay determination. This procedure followed the Hallimond Tube Flotation Test method (Wills & Finch, 2015). The captured mass and assay results from the tests works with 4E accountability of 100 ± 10%, were used to calculate the average weight of each test. Subsequently, an analysis of mass pull, concentrate grade and recovery, was done. A 1 745 g aliquot was placed into a rod mill. Raw water (1 428 mls) was then poured into the rod mill as make up water. The rod mill was run for 40 minutes to obtain 80% passing 75-micron screen particle size. Approximately, 1 026 mls of raw water was used to clean the rods and the slurry to produce a pulp of 55% solids. The pulp was then transferred to a three-litre float cell of a Denver D12 bench flotation machine. The pulp was agitated for three minutes at 1 450 rpm to ensure the slurry was homogeneous prior to reagent conditioning. The reagent dosage for flotation is detailed in Table 1. The agitator speed was then reduced to 1 200 rpm. The collector was added at the third minute and conditioned for four minutes. Depressant was then added and conditioned for one minute. Frother was also added and conditioned for one minute after which air was introduced. Concentrates were collected into three separate metal trays. Tray 1 collected scrapings for 15-seconds after a three-minute interval. Tray 2 collected scrapings for 15-seconds after a four-minute interval. And finally, tray 3 collected scrapings for 15-seconds after a five-minute interval. The three metal trays collected concentrates 1, 2 and 3, respectively. At the end of the flotation test the tailings remained in the cell. This procedure was followed for the flotation of pristine ore and oxidised ore.

Flotation Reagents

The collector, Sodium Isobutyl Xanthate (SIBX), was supplied by Frusina Holdings and prepared daily at a solution strength of 10 g/litre (1%wt). This collector is made up of 60% SIBX. The frother, SASFROTH 200, was supplied by Sasol Chemicals, and contains 70% 2-[2-(2-butoxyethoxy)ethoxy]ethanol and 15% diethylene glycol monobutyl ether. The frother was also prepared daily at a solution strength of 10 g/litre (1%wt). The depressant used for the test work, Celect SD, was supplied by Nasaco International Limited, and contains 80%

sodium carboxymethyl cellulose. It was prepared daily at a solution strength of 10 g/litre (1wt%). To prevent contamination, three syringes were used, one for each reagent. Reagent consumption for flotation tests on oxidised ore is shown in Table 1.

Table 1: Flotation tests reagents

Reagent g/t	NaHS	Collector	Depressant	Frother
Test 1	_	300	150	50
Test 2	50	300	150	50
Test 3	75	300	150	50
Test 4	100	300	150	50
Test 5	200	300	150	50

Sulphidisation Test work

The procedure for milling was followed to obtain the optimum grind for flotation. NaHS was used as a sulphidising agent. The NaHS used was in the form of flakes. The amount of reagents used is given in Table 1. NaHS was added after conditioning of the pulp for three minutes. The conditioning time after the addition of NaHS was 10 minutes, followed by the addition of the collector, depressant and frother. The procedure followed during the flotation of unsulphidised pulp was repeated to obtain concentrates and tails. Sulphidisation was done prior to flotation in a three-litre Denver flotation cell. Various test works were conducted with varying NaHS concentrations.

Results

This section provides the results for the experiments carried out on the oxidised ore, sulphidised oxidised ore and the fresh sulphide ore, as well as a detailed analysis of the results.

Fire Assaying Results

The ore was analysed for 4Es using fire assaying and the ICP-OES characterisation technique. The oxidised ore was found to be of low-grade at 2.9 g/t, as shown in Table 2. The Pd content is much lower than the Pt, indicating Pd remobilisation from the weathered zone to the lower zone that might reduce the flotation efficiency by changing Pt: Pd ratio. Pristine ore has an overall feed grade of 3.48 g/t, which indicates that the ore had a lower grade due to chemical changes. The ore is often subjected to weathering processes such as exposure to wind, rain and temperature variations, resulting in the breakdown and erosion of minerals, leading to loss of valuable components and an overall lower feed grade. Table 2 shows the results for the ICP analysis.

Table 2: 4E analysis of ore and pristine ore

Element	Ore g/t	Pristine Ore
Pt	1.65	1.86
Pd	0.89	1.21
Rh	0.30	0.34
Au	0.06	0.07
Total	2.90	3.48

Grinding Results

Figure 1 shows the percentage passing of grinds through a 75-micron screen, together with the time taken in the rod mill.

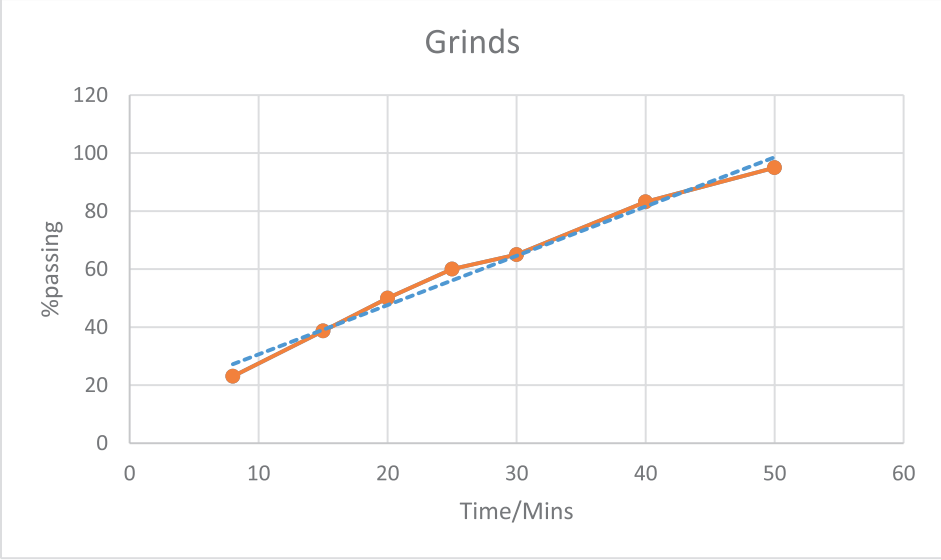


Figure 1: Grinds obtained with time

Samples of completely oxidised ore were grinded and wet-sieved using a 75-micron screen to note the time taken to reach 80% passing a 75-micron screen. The time taken to reach 80% passing a 75-micron screen, was 40 minutes.

Flotation Tests

NaHS was added ranging from 50 g/t to 200 g/t since pre-trial tests showed no significant changes for dosages between 0 g/t to 50 g/t. The relationship between float time and recovery for the flotation of pristine ore, oxidised ore and sulphidised-oxidised ore at different concentrations of NaHS is shown in Figure 2.

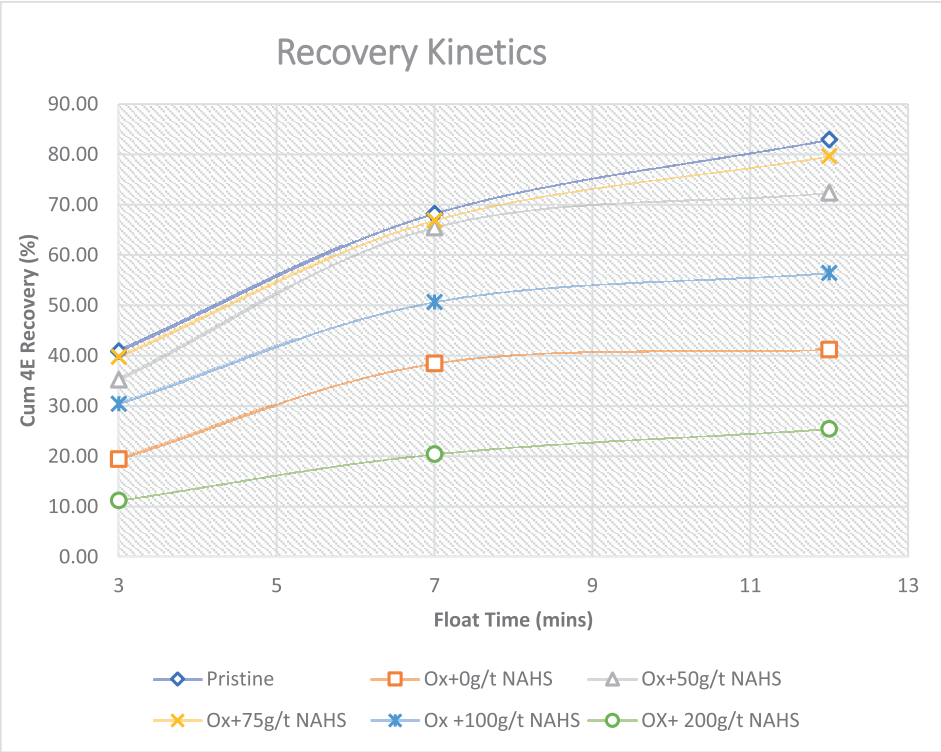


Figure 2: Recovery kinetics of the flotation test works

The graphs in Figure 2 show that cumulative recovery is generally increasing with time. Cumulative recovery is equal to recovery from tray 1 + tray 2 + tray 3. This is because the reaction kinetics increase with time as flotation reagents get enough time to interact with minerals and become fully activated. The reagents have more time to interact with the ore particles, thus enhancing their effectiveness and leading to improved recovery rates. The highest rates were obtained on pristine, owing to the fact that the ore is sulphide in nature, hence it easily interacts with the sulphide flotation reagents. Recovery increased from 50 g/t to 75 g/t, but decreased at 100 g/t to 200 g/t due to over-sulphidisation which has a depressing effect on the required material. Oxidised ore from the open pit at 75 g/t of NaHS had a performance which is close to pristine. This shows that sulphidisation was effective during that test work. The open pit ore which is completely oxidised and did not go through the sulphidisation process had very slow rates of increasing recovery. It was observed during flotation that the oxidised ore forms very small and unstable bubbles and thus did not float. This shows that the flotation kinetics were very slow due to limited accessibility to valuable minerals. The oxide layer inhibits the interaction of the pulp with reagents, resulting in slow reaction kinetics. Sulphidisation of the oxidised ore generally increased the reaction kinetics of

oxidised ore. Recovery improved from 40% to 80% through the sulphidisation process.

Concentrate Grade

The relationship between float time and concentrate grade for the flotation of pristine ore, oxidised ore and sulphidised ore at different concentrations of NaHS is shown in Figure 3.

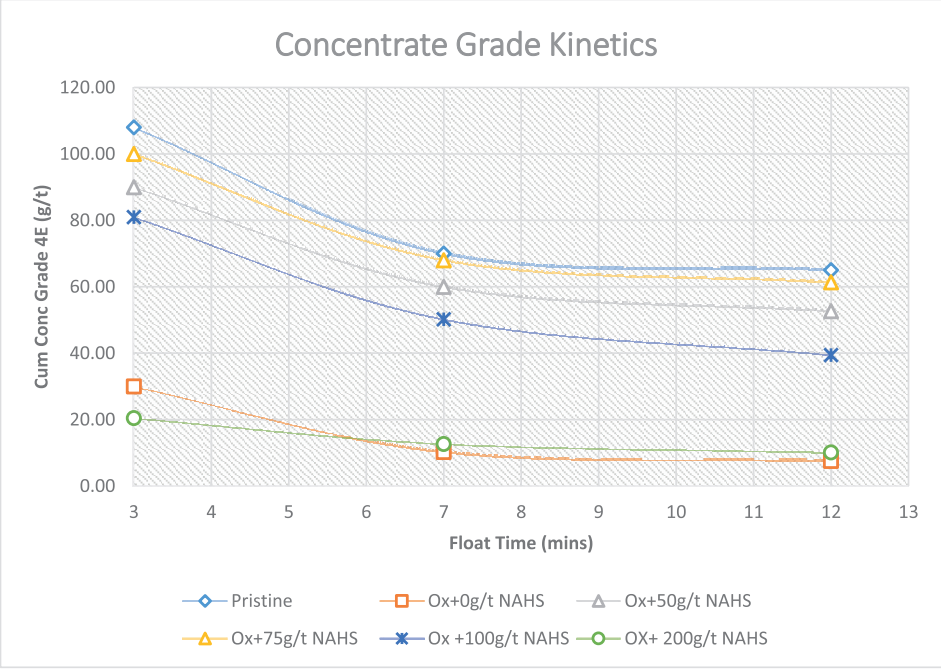


Figure 3: Concentrate grade kinetics

The grade generally decreased with time. The highest grade was obtained in the first three minutes. The concentrate grade of oxidised ore increased from 30 g/t 4E to 100 g/t 4E through sulphidisation. The concentrate grade increased after the sulphidisation of the ore using 50 g/t to 75 g/t of NaHS. The highest concentrate grade was achieved at 75 g/t of NaHS. The concentrate grades obtained at 75 g/t were almost the same as that of fresh ore (pristine). Excessive NaHS can lead to over-activation of minerals which causes them to be more easily entrained in froth, resulting in inclusion of gangue material in concentrate, thus leading to lower grades (Wills & Finch, 2015).

Grade and Recovery

Figure 4 shows the grade and recovery of all the flotation test works which were carried out on pristine ore, oxidised ore and sulphidised oxidised ore, as well as the mass pull.

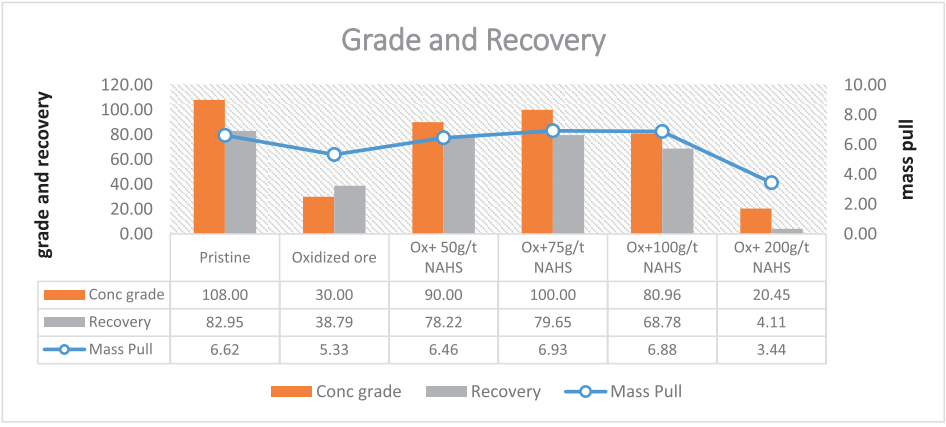


Figure 4: Grade vs recovery

The sulphidisation from 50 g/t to 100 g/t generally improved the grade and recovery of oxidised ore. The mass pull of open pit ore was lower than that of sulphidised ore. Sulphidisation at 200 g/t had the lowest mass pull as well as grade and recovery. Pristine had the highest grade and recovery. Mass pull was varying in different test works due to inconsistent scrapping, but is generally higher for pristine and successfully sulphidised ores.

Discussion

The addition of NaHS at 50 g/t, 75 g/t and 100 g/t resulted in an increase in both grade and recovery. The mechanisms for sulphidisation involve the adsorption of hydrosulfide ions onto the oxidised mineral surface, followed by formation of a sulfide surface through anionic exchange (Castro *et al*., 1974). This indicates that the sulphidisation process was effective in improving the overall quality and quantity of the desired product. The recovery improved from 40% to 80%, and the grade also improved from 30 g/t to 100 g/t 4E. The oxidised ore on its own resulted in poor flotation recovery that is indicated by very low mass pull, as small bubbles with a lot of liquid were scrapped off into the tray. Sulphidisation resulted in more stable bubbles and increased mass pull as solids were being recovered. However, the decrease in grade and recovery observed when the NaHS dosage was increased from 100 g/t to 200 g/t is an interesting finding. There could be several factors contributing to this observation. At higher dosages of NaHS, the sulphidisation reaction becomes too strong, leading to over-sulphidisation of the ore particles. This excessive sulphidisation resulted in the formation of unwanted sulphide compounds or the coating of valuable minerals, thereby reducing their availability for recovery. Controlled potential sulfidisation (CPS) reduces the chances of excessive sulphide concentration in the pulp, and is extensively employed in the flotation of base metal oxides like copper and lead oxidic ores (Jones & Woodcock, 1978; John, 1991). The higher dosage of NaHS caused excessive froth formation during the flotation process. This led to the entrainment of valuable minerals in the froth, resulting in a lower recovery. Different ores may

have varying responses to the sulphidisation process, and the optimal dosage of NaHS may vary accordingly. Floatability of completely oxidised ore was restored because 80% flotation recovery was achieved while unsulphidised ore had poor flotation kinetics. Hence, it is suggested that controlled sulphidisation could be a viable technique of improving flotation recovery of oxidised PGM ores (Newell *et al*., 2007).

Conclusion

From the test works that were carried out, it can be concluded that oxidised PGM ores are not amenable to flotation as shown by the low recoveries of 40%. The study was carried out to determine the applicability of sulphidisation as a pre-treatment method on the oxidised PGMs ore. The results of the study show that the ore can be pre-treated using the sulphidisation technique to improve flotation recoveries as evidenced by the increase in recovery from 40% to 80%. The process is more efficient at a dosage of 75 g/t of NaHS. Sulphidisation should, however, be carefully controlled to prevent over-activation of the pulp, which has negative effects on the recovery.

Furthermore, attention needs to be paid to the following:

1. Sulphidisation has a potential to improve the flotation kinetics. However, reagent dosage should be monitored.
2. Further tests should be conducted to investigate the effect of other sulphidisation agents such as Na_2S and the use of biological sulphidisation agents.
3. The activation mechanism of the sulphidisation process also needs to be determined as well as the stability of reagents.

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