Abstract—This study investigated the effect of pH on the recovery and grade of the Platinum Group Metals (PGMs) and base metal sulphides from the UG2 ore of the Bushveld complex. This was achieved through running a series of test work in a Denver flotation cell at varying pH 6-11 at constant reagent dosage. The UG-2 reef is characterized by two predominant gangue phases i.e. chromite and silicate, that have significantly different physical and chemical properties. The test work was aimed at evaluating which pH gives best recoveries, and finding the effect of the chrome content in these recoveries. A pH of 9 gave the highest recovery compared to other pH ranges. However, the highest PGM grade was attained at a pH of 6 which is slightly acidic. Ideally this trend could be expected since the collectors (xanthates) are more stable in alkaline medium. The higher PGM recovery was also accompanied by higher chrome content as a result of their similar chemical properties.

Keywords- Metal sulphides, gangue phases, recoveries, Platinum Group Metals, Bushveld complex

I. INTRODUCTION

This article concentrates on the effect of pH on the recovery and grade of PGMs from UG2 ore by flotation. Flotation is a process of separating minerals from one another: this technique depends primarily on the difference in the wettability of the particles. This concept is broad and researchers continuously carry out test works to find optimum conditions to improve both grade and recovery of PGMs. Flotation depends on a number of factors which include particle size, pulp density, reagent dosage and pH. In practice, selectivity in complex separation is dependent on a balance between reagent dosages and pH [1]. Thus reagents and pH should be delicately balanced to achieve optimum recoveries and grade. Previous studies on the flotation of base metal sulphides mainly focused on reagent optimization to achieve optimum recovery and grade [2]. In this study the effect of pH and its balance with reagent dosages is examined with the intention of improving flotation performance. The Bushveld complex which is the world’s largest known source of PGMs with very complex sulfides and PGMs mineralogy was studied in this work. Depending on the type of reef and geography the Bushveld complex is the predominant PGM mineral types and their association and can vary to a great degree [3].

There are about fourteen type locality platinum minerals that have been discovered in the Bushveld deposit. There are also 150 unnamed and, the most part, inadequately characterized platinum group phases recorded from the Bushveld complex. Over 50% of these unnamed minerals are documented from the UG2 chromite, majority of which are platinum phases. The UG2 layer is the host unit of most Bushveld minerals such as Iridium, Osmium, Rhodium, Ruthenium, Platinum and Palladium [4]-[7].

A. Mineralogy of the UG2 Ore Body

The UG2 ore is a platinum-bearing chromite rich ore that contributes a growing proportion of platinum group metals production from the Bushveld Ingenious complex. This ore is ideal for study of entrainment as it contains two major gangue phases which are chromite and pyroxene that are significantly different in chemical and physical properties however, poses certain problems and challenges. High recovery of valuable minerals from UG2 is accompanied by high chrome recoveries to the concentrate and this is detrimental to the downstream smelting process. This is due to spinal formation, which is an insoluble species in respect to the conditions that prevail in the smelters. Furthermore, these species are of intermediate density (between matte and slag) and form a mushy layer at the matte-slag interface.

The UG2 ore consists mainly of chrome of about (60-90%) and Cr₂O₃ content averages of 43.5%. The dominant base metal sulphides are mainly pentlandite and chalcopyrite, with lesser pyrrhotite, pyrite, arsenopyrite, bornite chalcocite, covellite galena and millerite. Approximately 85% of base metal sulphides are present at grain boundaries, 4% occur within chromite and the remainder occurs within silicates grains. In general the PGM assemblage of UG2 chromite is dominated by Pt-Pd sulphides (35%) and laurite (30%) with Pt-Fe alloy and intergrowths (21%), Rh sulphide (11%) and Pd alloys (3%).
B. Froth Flotation

Flotation is a physico-chemical process which exploits the differences in the electrochemical properties of mineral surfaces. All minerals are soluble in water to some extent, which results in the formation of an ‘electrical double layer’ at the mineral surface. Flotation depends directly on the nature and properties of mineral-water interface. Two factors are important: (1) the interaction of water molecules with the mineral surface, both in liquid and gaseous environments, and (2) the electrical double layer at solid-water interface [7]. The addition of flotation reagents selectively renders the surfaces of mineral particles either hydrophobic or hydrophilic as a result of the ionic interactions and exchanges that can occur at the double layer. The hydrophobic particles become attached to air bubbles and are carried upwards through the slurry to a froth layer that forms at the top of the flotation cell. This froth layer is removed and usually becomes the concentrate. Hydrophilic particles remain in the slurry in the flotation cell.

Most minerals are naturally hydrophilic i.e. polar in molecular structure and they need collectors to render them hydrophobic (non-polar in molecular structure). Collectors are heterogeneous compounds with a functional inorganic group and a hydrocarbon chain. There is a difference in electric charge on the ends of the inorganic group caused by an uneven distribution of polar bonds on its ends. The hydrocarbon chain is non-polar and has no difference in charge between its ends. The inorganic group is the portion which adsorbs on the mineral surface (provides hydrophobicity), causing the mineral to attach itself to the bubble. The most common mineral types that are recovered this way are sulphides and the widely used sulphide collectors are sodium and potassium salts of certain acids containing a hydrocarbon group. These are anionic collectors and include xanthates and dithiophosphates [8] – [10]. The use of co – collectors or promoters in flotation is well established [11].

One of the most important aspects of froth flotation is the formation of a froth in which the valuable minerals are retained for further up grading. Thus the presence of a surface-active or frothing agent, either as a neutral frother or in the dual function as collector and frother, is vital to the process [8]. When mineral surfaces have been made hydrophobic by the use of a collector, they have to attach to a stable air bubble for them to be recovered. The stability of the bubble depends on the type of frother used. A good frother should have no collecting power but should be stable enough to ensure that the floated minerals are transferred from the float cell to a collecting launder [9]. Frothers are heteropolar organic reagents which are capable of being adsorbed on the air-water interface. The heteropolar structure of the frother molecules makes non-polar group to orientate towards air and the polar groups towards water. Frothers must be to some extent be soluble in water, otherwise they would be distributed very unevenly in an aqueous solution and their surface-active properties would not be fully effective. The alcohols (OH) are the most widely used frothers, since they have practically no collector properties, and in this respect are preferable to other frothers, such as the carboxyls, which are also powerful collectors [9].

During froth flotation the ore is crushed and ground to a specific size sufficient for mineral liberation. The ore is then suspended in slurry and mixed with reagent or collectors. The collectors react with sulphide mineral particles to make them hydrophobic. The treated ore is introduced to a water-filled aeration tank and a frother (usually alcohol based) is added. Air is then induced and the air bubbles attach to the hydrophobic minerals are skimmed off. These skimming are generally subjected to a cleaner-scavenger cell to remove excess silicates and to improve the grade of the final product which is sent for downstream processing [9].

C. Importance of pH

It is evident that from the fore going that pulp alkalinity plays a very important though the very complex role in flotation. In practice, selectively the separation is dependent on a delicate balance between reagent concentration and pH. Flotation where possible is carried out in a alkaline medium, as most collectors including xanthates are stable under these conditions [1].

The alkalinity of the pulp is maintained by addition of lime to a lesser extent sodium hydroxide or ammonia. The lowering of the pH can be attained by the addition of sulphuric acid or sulphurous acid. These chemicals are often used in very significant amounts in almost all flotation operations [9]. The pH regulators are cheaper than the frothers and collectors, however the overall costs is generally hither with the pH regulators per ton of ore treated. For example: the cost of lime in sulphide minerals flotation is roughly double the amount of the collector used, so the significant operation cost saving can be attained by proper selection of the pH regulators [1].

Lime being the cheapest, is widely used to regulate pulp alkalinity and used in the form of milk of lime, a suspension of calcium hydroxide particle in a saturated aqueous solution. Lime or soda ash is often added to the slurry prior to flotation to precipitate heavy metal ions from solution. In this sense the alkali is acting as “deactivator” as these heavy metal ions can activate sphalerite and pyrite and prevent their selective flotation from lead or copper minerals. Since the heavy metal precipitated by the alkali can dissociate to a limited extent and thus allows ions into solution, cyanide is often used with the alkali to complex them.

II. MATERIALS AND METHODS

A. Ore Preparation

The UG2 ore was crushed in stages using a laboratory jaw and cone crusher to 45% passing 75 µm. The crushed ore was then blended and rotary split to 1kg representative
sub-samples for the test work.

B. Experimental procedure

The test work was carried out in a Denver flotation cell of 1 kg capacity. All tests were conducted using the standard flotation procedure. The milled ore was then agitated in a Denver machine to ensure homogenous suspension of solids. Reagents specific to each test were added and conditioned as illustrated in Table 1, thereafter air was manually induced using an air rotameter. The concentrates were collected by manually scraping the froth using scraper blades. Either sulphuric acid or lime was used to achieve the desired pH. The flotation studies were performed at pHs of 6, 8, 9, 10 and 11. To ensure reproducibility the runs were carried out in quadruplets. The runs were carried out in 4 batches. Sulphuric acid and lime were added in a proportion so as to achieve the desired pH. The following pHs were studied 6.0, 8.0, 9.0, 10.0, 11.0. The pH prior flotation was measured; sulphuric acid or lime was used as a pH regulator added to get the desired pH.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Time (min)</th>
<th>SIBX (g/l)</th>
<th>S-acol (g/l)</th>
<th>M47 (g/l)</th>
<th>LF 230 (g/l)</th>
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<tbody>
<tr>
<td>Condition 1</td>
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<td>40</td>
<td>40</td>
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</tr>
<tr>
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<td>10</td>
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<tr>
<td>Float 1</td>
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<tr>
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<td>40</td>
<td>10</td>
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<td>5</td>
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</table>

C. Sample Preparation and Analysis

After flotation, wet samples were dried in an oven, then weighed and lump broken. Concentrates and tailings were put in separate packages to avoid contamination and these were analyzed for PGMs.

III. RESULTS AND DISCUSSION

Fig. 3 shows PGMs recovery versus cumulative recovery. The highest grade was achieved at pH of 6 while the highest recovery was realised at a pH of 9. According to Wills [1], the pulp alkalinity plays a very important role in flotation. Xanthate which is the collector used in this work is stable in alkaline medium. It selects mineral water repellent by adsorption of molecule or ions to the mineral surface [1]. The grade and recovery of PGMs are at the lowest values at a higher pH of 11. This is because the collection capacity of xanthates is reduced when they become more stable at higher pH values. Wills [1] emphasized the balancing of reagents suites with pH for maximum activation for all reagents to achieve both high grades and recoveries.

![Fig. 3. PGMs grade versus cumulative recovery](image)

![Fig. 4. Chrome grade versus recovery](image)

UG2 ore has a lot of chrome content with similar chemical properties to those of the PGMs and base metals. During flotation the amount of chrome recovered with PGMS need to be minimized to avoid smelter feed containing high chrome content. The relationship between chrome grade and recovery is shown in Fig. 4. Highest chrome grades are achieved at pH of 11 whilst the highest recovery is at pH of 9. High recoveries for both PGMS and chrome were achieved at pH of 9 supporting the theory that higher PGMs recovery is coupled with high chrome recoveries. The high recovery of valuable minerals from UG2 ore accompanied by high chrome recoveries to the concentrate is detrimental to the downstream smelting process. This is due to spinal formation, which is an insoluble species in respect to the conditions that prevail in the smelters. In addition, these species are of intermediate

**TABLE I**

<table>
<thead>
<tr>
<th>Milling</th>
<th>Condition</th>
<th>Time (min)</th>
<th>SIBX (g/l)</th>
<th>S-acol (g/l)</th>
<th>M47 (g/l)</th>
<th>LF 230 (g/l)</th>
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<tr>
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<tr>
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</table>
density (between matte and slag) and form a mushy layer at the matte-slag interface [6]. For effective flotation of valuable minerals, gangue materials in the pulp should be depressed. This is complicated as certain silicate gangue phases are activated in alkali solutions [15].

Fig. 5 shows recovery versus time relationship. The highest and lowest recoveries with time were achieved at pHs of 9 and 11 respectively.

The recovery of copper and nickel at various pHs is represented in fig. 6. Highest recovery was achieved at pH of 6 indicating that the recovery of base metals is favoured by acidic conditions. About 40% of the recovery was achieved at pH of 6 compared to about 10% at pH of 11. As discussed above the high grade of PGMS attained at low pH is accompanied by high recovery of base metals.

IV. CONCLUSION

This work demonstrated the importance of pH and its balancing with reagent dosages to improve both recovery and grade. In future studies it is recommended to widen the pH range and to find ways of reducing high chrome recoveries associated with high PGM recoveries. The recovery behaviour of chrome with time and its dependence on pH was found to be similar to that of PGMS. The results of this work can be used to optimize industrial flotation plants.

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REFERENCES