

Received April 20, 2018; reviewed; accepted June 4, 2018

## A review of investigations into the management of gangue in the flotation of platinum group minerals

Cyril O'Connor<sup>1</sup>, Jenny Wiese<sup>1</sup>, Kirsten Corin<sup>1</sup>, Belinda McFadzean<sup>1</sup>

<sup>1</sup> Centre for Minerals Research, Department of Chemical Engineering, University of Cape Town, Private Bag Rondebosch 7701, South Africa

Corresponding author: [cyril.oconnor@uct.ac.za](mailto:cyril.oconnor@uct.ac.za) (Cyril O'Connor)

**Abstract:** The Bushveld Complex of South Africa contains almost 90% of the world's reserves of platinum group minerals (PGMs). In the flotation of PGMs, there are significant challenges arising from the need to treat ever-decreasing grades of the relevant ore deposits. The major challenge in the flotation of these ore bodies is the control and management of the gangue minerals, particularly silicates such as orthopyroxene, plagioclase feldspar, and pyroxene which are often rimmed with talc which makes them naturally floatable. It has been shown that various polysaccharide depressants such as CMC and guar have different properties in terms of depressing the gangue minerals. Since the PGMs are often associated with sulphides, copper sulphate is widely used as an activator in PGM flotation but can inadvertently activate the gangue minerals as well as reduce the recovery of PtTe<sub>2</sub> which accounts for up to 40% of the Pt in the Platreef ore body. Depressants also reduce the mass of solids reporting to the froth and can thus destabilize the froth. This effect on the froth can be mitigated by using higher frother dosages or water of higher ionic strength. In summary due care needs to be taken to carry out site test work to develop an optimum ratio of collector, frother, activator and depressant to ensure that the highest grades and recoveries of the PGEs are obtained while reducing depressant dosage as much as possible. Chromite recoveries can be reduced through the application of gravity separation or reducing entrainment through reduced water recovery.

**Keywords:** platinum group minerals, depressants, copper sulphate, chromite

### 1. Introduction

The Bushveld Complex located in the north of South Africa contains the world's largest deposit of Platinum Group Minerals (PGMs). The so-called upper Critical Zone of the Complex hosts the largest concentration of platinum group elements (PGEs) in the world. The Zone hosts the Upper Group Chromitite No.2 (UG2) and Merensky Reef as well as the Platreef mineralisation of the northern limb of the Bushveld Complex. The Merensky pegmatoid Zone contains the base metal sulphide grains and associated PGMs. Of particular importance to the topic of this paper is the occurrence in these reefs of various gangue minerals. The Merensky Reef consists predominantly of orthopyroxene (~60%), plagioclase feldspar (~20%), pyroxene (~15%), phlogopite (5%) and occasional olivine. Secondary minerals such as talc, serpentine, chlorite and magnetite have widespread occurrence. Of these, talc is the only mineral to show significant natural floatability (Feng et al, 2012; Douillard, 2007). Although present in small amounts talc is closely associated with pyroxene and imparts significant floatability to the high concentrations of pyroxene present in these ores (Becker et al, 2009). The base metal sulphides consist predominantly of pyrrhotite (~40%), pentlandite (~30%) and chalcopyrite (~15%). The major platinum group minerals are cooperite (PtS), braggite [(Pt,Pd)NiS], sperrylite (PtAs<sub>2</sub>) and PGE alloys. The UG2 consists predominantly of chromite (between 60 – 90% by volume) with lesser silicate minerals (5 – 30% pyroxene and 1 – 10% plagioclase). Other minerals present in minor concentrations, can include silicates, oxides and base metal sulphides. Total PGE varies from locality to locality, but on

average range between 4 and 7 g/t. The PGMs present in the UG2 Reef are highly variable, but generally the UG2 is characterised by PGE sulphides such as laurite ( $\text{RuS}_2$ ), cooperite ( $\text{PtS}$ ) and braggite  $[(\text{Pt},\text{Pd})\text{NiS}]$ . The base metal sulphides consist predominantly of chalcopyrite, pentlandite and pyrrhotite. The Platreef is located in the northern limb of the Bushveld Complex. This reef consists of a complex assemblage of rock types, with pyroxenites, serpentinites and calc-silicates being the most abundant. Base metal mineralisation and platinum group element (PGE) concentrations are found to be highly irregular, both in value as well as in distribution. The predominant platinum group minerals (PGM) in the mined area of the Platreef are the PGE tellurides, alloys, arsenides and sulphides. The Pt and Pd tellurides are the most important and contribute to around 20-30% and up to 45% of the PGMs present in the Platreef ore followed by the alloys (26%), arsenides (21%) and sulphides (19%) (Schouwstra et al., 2000).

Flotation is used for concentrating sulphide and PGE minerals at PGM concentrators. With the ever-decreasing grades of the ore deposits it has now become necessary to treat low-grade complex polymetallic ores. Moreover, due to the need to enhance liberation there is an increased need to process fine particles that are relatively more difficult to float. Given the mineralogy of the ore body it is self-evident that the major challenge in the flotation of these ore bodies is the control of the gangue minerals, both the silicates and the chromitite.

This paper presents results obtained in an extensive programme of testwork investigating the influence of various factors on the behaviour and control of the gangue minerals during flotation. These factors include the use of different types of depressants, the interactive effects between various collectors, frothers and depressants, the effect of different ions present in the process water on the depression of the gangue minerals, and the effect of using depressants on the behaviour of the froth.

## 2. Materials and methods

### 2.1. Ore

As indicated above the PGMs occur in different zones of the Bushveld Complex. In the experimental programmes described in this paper the ores used were from the Merensky, UG2 and Platreef bodies. In the results section the type of ore used in the various tests is indicated.

### 2.2. Flotation procedure

In all experiments synthetic water of approximately the composition shown in Table 1 was used. This equates to an ionic strength of approximately  $3.5\text{E-}02$ . The composition developed by the AngloAmerican Platinum researchers (Shackleton et al., 2007a) approximates that of the process water generally used on the PGM concentrators treating these ores.

Table 1. Composition of the synthetic plant water used in these investigations  
(TDS = 1023 ppm; ionic strength = 0.0213 M)

Ions	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{NO}_2^-$	$\text{CO}_3^{2-}$	TDS
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Concentration	80	70	153	287	240	176	-	17	1023

After milling in a laboratory scale rod mill the slurry was transferred to a 3 L Barker flotation cell, where the volume was made up using synthetic plant water to produce 35% solids. The cell was fitted with a variable speed drive and the pulp level was controlled manually by the addition of synthetic plant water keeping the froth height constant at 2 cm. The impeller speed was set at 1200 rpm. The air was maintained at a flow rate of 7 L/min in all the tests. Four concentrates were collected at 2, 6, 12 and 20 min of flotation time. Water and solids recoveries were measured for each test. Feeds, concentrates and tails were filtered, dried and weighed before analysis. Elemental analysis of samples was done after acid digestion using an Atomic Absorption spectrophotometer. Sulphur analysis was carried out using a LECO sulphur analyser. PGM assays were carried out in a commercial laboratory. Due care was taken, through repeat tests, to check on reproducibility of all experiments and analyses.

### 3. Results and discussion

#### 3.1. Comparing the performance of guar and CMC as depressants

Depressants are used to reduce the extent to which naturally floating gangue (NFG) present in the ore reports to the concentrate. The most commonly used gangue depressants are polysaccharides such as modified guar gum and carboxymethylcellulose (CMC). Polysaccharides are made up of sugar monomers bonded together differently (Laskowski et al, 2007). Guar gum belongs to the galactomannan group and is a branched polysaccharide. The structure of this polymer is such that it is soluble without the introduction of charged sites into the molecule and therefore the modified guar has very low degrees of substitution (DS) and on adsorption reduce the charge on the particles. CMC is a cellulose derivative. The DS of the carboxymethyl groups is high ( $\sim 0.7$ ) and on adsorption can lead to the development of a high negative charge on the particles and result in strong dispersion. It is important to note that the cost associated with the use of depressants often exceeds that of any other reagents used in the flotation process. Because of its natural hydrophobicity most of the fundamental studies on the use of depressants to reduce the recovery of naturally floating gangue (NFG) minerals have been carried out on talc. The adsorption of depressants onto talc have been extensively reported in literature (e.g. Parolis et al., 2002 and 2008; McFadzean et al, 2011). Steenberg and Harris (1984) and Shortridge et al. (1999) have shown that guar adsorbs more strongly onto talc than does CMC.

McFadzean et al. (2011) has studied the relative effectiveness of CMC and guar in depressing gangue minerals at different dosages and with different average molecular weights using a Merensky ore. The high molecular weight depressants ranged between 600,000 - 700,000 g/mol and the low molecular weights between 40,000-70,000 g/mol. The depressants were tested using microflotation, batch flotation and equilibrium adsorption studies. The investigation showed that, at so-called starvation dosages (e.g.  $\sim 100$  g/t) the high molecular weight polymers did not depress naturally floating gangue (NFG), whereas the low molecular weight depressants did. At relatively higher dosages (e.g.  $\sim 300$  g/t), both high and low molecular weight polymers essentially depressed all NFG, without reducing sulphide recovery. High molecular weight depressants appeared to be more selective towards hydrophilic gangue (pyroxene and feldspar) at starvation dosages in batch float experiments. This was inferred due to the fact that, even though all the polymer was adsorbed from solution, the naturally floating gangue was not depressed by high molecular weight polymers at 100 g/t dosages. In addition, there was a marked reduction in froth stability when using the high molecular weight polymers, which was attributed to the more selective adsorption of the polymer on the fine pyroxene and feldspar, resulting in slime cleaning of the sulfides. At 300 g/t dosages, all polymers act as good depressants of the naturally floating gangue. None of the polymers depressed the sulphides in the pulp zone. It was shown that at depressant dosages of 100-300 g/t, adsorption densities range from 20% to 50% pseudo-monolayer coverage. In another study it was shown that the shorter chain lengths within a distribution in large molecular weight depressants were preferentially adsorbed. The low molecular weight depressants were adsorbed across the entire molecular weight range, but still showed some preferential adsorption of the shorter chains (McFadzean and Groenmeyer, 2015). It has also been shown (Corin and Harris, 2010) that no benefit is gained from the blending of the depressants guar and CMC. At all depressant dosages used, the blended depressants favoured the weaker of the two pure depressants, viz. guar at low dosages ( $<200$  g/t) and CMC at higher dosages ( $>200$  g/t). The use of blends, as was shown for pure depressants, did not affect the recovery of either copper or nickel sulphides.

With respect to the relative adsorption of depressants onto various gangue minerals, Mhlanga et al. (2012) observed that in a buffered solution, talc had the highest affinity for guar, followed by chromite, pyroxene, then plagioclase. This progression in the affinity for guar in a buffered solution correlated with the differences observed in the surface charge of each mineral at pH 9 as determined in zeta potential measurements. These observations are also consistent with the acid/base interaction theory of Laskowski et al. (2007) since talc, pyroxene and chromite had the most basic surfaces, hence the highest affinity for guar, and plagioclase, which had the most acidic surface, would have the weakest interaction with guar. This study also showed that in a binary mixture of each mineral with talc, guar adsorbed preferentially onto pyroxene, chromite and talc, with limited adsorption onto plagioclase. This

means that, in industrial applications, large quantities of depressant may be wasted in adsorption onto minerals such as pyroxene and chromite, which are naturally hydrophilic.

Given the relative high cost of depressants the effect of dosage on their performance is of importance. Fig. 1 shows the mass of naturally floating gangue (NFG) viz. gangue which is naturally hydrophobic and which can be depressed by using either CMC or guar as depressants, for different dosages of either guar or CMC in a study of two ore samples from the Merensky reef (Wiese et al, 2007). Also shown is the effect of the presence of copper sulphate which will be discussed later. As shown in this Fig. increasing the dosage of either depressant to about 300g/t almost entirely depressed the recovery of any NFGs. In general guar tended to be relatively more effective in this regard than CMC.

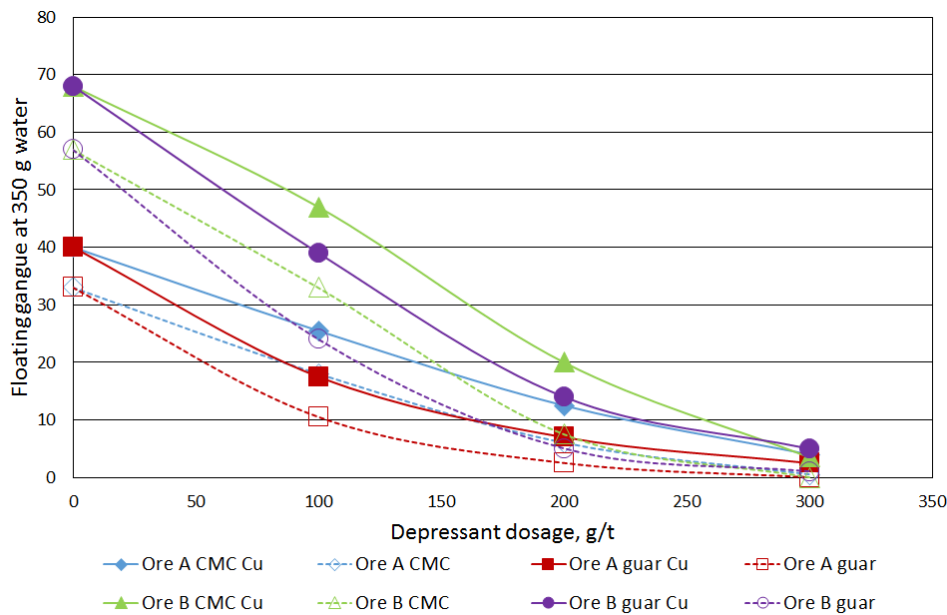


Fig. 1. Naturally floating gangue (NFG) recovered at 350 ml water recovery for Merensky ores using different dosages of CMC or guar in the presence or absence of copper sulphate (Wiese et al, 2007)

Although the amount of NFG still floating was small it is speculated that this may be due to the fact that these gangue minerals are present as composites with sulphide minerals. An important ramification of this investigation was that it was now possible to determine the amount of entrained gangue, viz. those minerals which do not respond to depressant treatment and report to the concentrate through entrainment by using depressant dosages of about 300g/t.

### 3.2. Effect of depressants on froth behaviour

One of the unintended consequences of depressing the NFG through the use of depressants is that the mass of solids reporting to the froth is significantly reduced and this has negative consequences in terms of the stability of the froth. Fig. 2 (Wiese et al, 2010) shows that for both guar and CMC at an equivalent frother dosage the presence of the depressant results in lower water and solids recovery. It has been proposed that the amount of water recovered is an indicator of the froth stability (McFadzean et al, 2016; Neethling et al, 2003) and hence this Fig. suggests that depressants have a negative effect on froth stability. This Fig. also shows that this can be partially overcome by increasing the frother dosage.

As indicated above, one option to overcome the negative effect of depressants on froth stability is to increase frother dosage. Since increasing ionic strength is also known to enhance froth stability, Corin and Wiese (2014) studied the effect of both ionic strength and frother dosages on solids and water recoveries as well as on copper and nickel grades and recoveries using a Merensky Reef ore sample. It was observed that at low ionic strength (i.e. deionized water) increased frother dosages increased the amount of NFG and entrained gangue recovered and this is consistent with the increased water and solids recoveries observed. Clearly it is critical to carefully balance the relative effects of frother and depressant dosages. Although the depressants may reduce froth stability through reduced mass of

solids reporting to the froth, Schreithofer et al. (2011) in a study of the foaming properties of the frother, Dowfroth 200, in the presence on the effect of a modified guar and a CMC, has shown that depressants in fact enhanced froth formation, but the mechanism of action is different. The CMC depressant appeared to act more through increasing bulk viscosity, while the guar has more influence on the surface rheology. These phenomena may be attributed to formation of surfactant-polymer complexes in the solution. Clearly there are two competing influences, viz. the loss of froth stability to the reduced amount of solids present in the froth and increased froth stability due to a frother-depressant interaction. It is likely that the loss of solids will have the overriding influence on froth stability, since reduction in froth stability was observed in the presence of both frother and depressant.

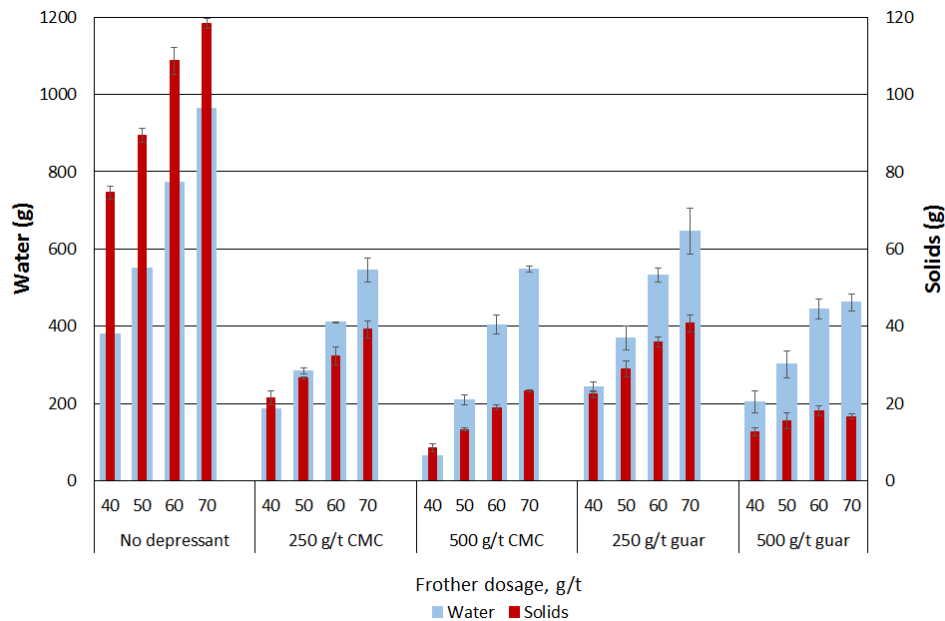


Fig. 2. Effect of depressant type and dosage and of frother dosage on mass of water and solids recovered (Wiese et al. 2010). Error bars show standard error between duplicate tests

### 3.3. Interaction between collectors and depressants

The interaction between xanthate collectors and depressants has been investigated. It was found that at low depressant dosages sodium isobutyl xanthate (SIBX) always resulted in lower froth stability than sodium ethyl xanthate (SEX) whereas using sodium diethyl dithiophosphate (DTP) resulted in increased froth stability (Wiese et al., 2005b). Fig. 3 (Corin et al., 2012) shows that DTP caused an increase in the recovery of fine particles (<25  $\mu\text{m}$ ) and this may explain the increased froth stability. This finding may have important ramifications for Pt and Pd recoveries in the treatment of ores where significant amounts of these elements are contained in the <25  $\mu\text{m}$  fraction and for ores which are subjected to ultrafine grinding.

Moimane et al. (2016) in a factorial design investigation showed that there are a number of significant interactions occurring between depressant and frother, frother and ionic strength, as well as collector and depressant. These are important when selecting reagent suites because different flotation responses will be obtained as a result of different interactive effects of the variables. For example, nickel recovery was slightly improved at low depressant dosage by increasing frother dosage but this did not occur at high depressant dosage.

### 3.4. Effect of ions in the water on the depression of gangue minerals

In the work being reviewed in this paper the effect of salts/ions present in the process water on the activity of the depressants was investigated. Laskowski et al. (2007) have shown that non-hydrolyzable metal cations can affect the adsorption of polysaccharides such as CMC or guar onto a strongly acidic

surface such as quartz. For example, water structure breakers such as  $K^+$  and  $Cs^+$  will significantly increase their adsorption while water structure makers such as  $Na^+$  and  $Li^+$  do not affect the adsorption.

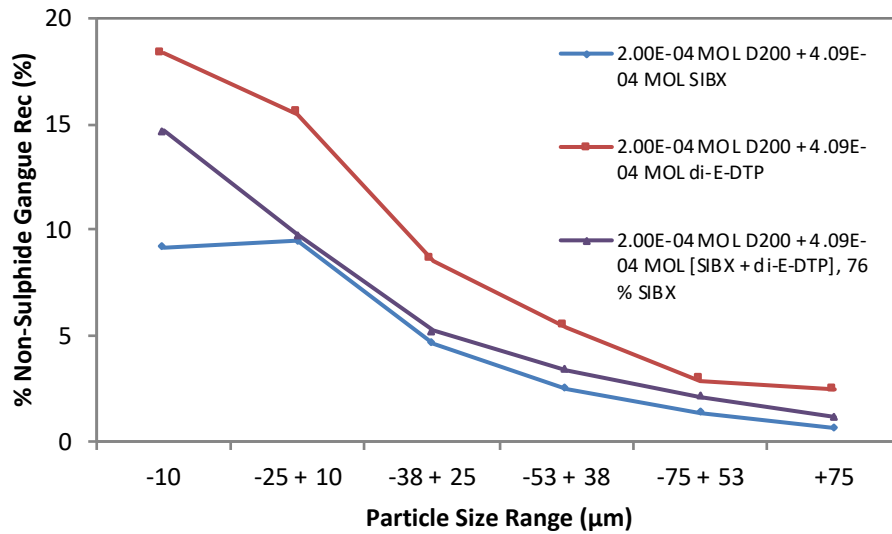


Fig. 3. Recovery of non-sulphide minerals by size class using SIBX, diethyl DTP and a 76:24 M mixture of these reagents. Frother in all cases was Dowfroth 200 at a total molar concentration of  $2.00E-04$ . Molar concentrations are indicated (Corin et al., 2012)

In this context one of the most important such species is copper sulphate. Many PGM concentrators use copper sulphate as an activator since it is assumed that this will promote the recovery of PGMs which are associated with sulphide minerals. Fig. 1 showed the recoveries of NFG at different dosages of CMC or guar in the presence or absence of copper sulphate for both ore samples. It can be seen that the presence of copper sulphate always resulted in higher recoveries of the gangue minerals. It has also been shown, in an investigation using XPS and ToF SIMS (Shackleton et al., 2003), that copper sulphate resulted in significant inadvertent activation of gangue minerals such as pyroxene confirming the observations shown in Fig. 1. It was shown that it was possible to reverse this effect by using an amine such as ethylenediamine. It was postulated that this was because of the amine complexing with copper ions in solution thus affecting the equilibrium between copper ions on the surface of the pyroxene and in solution.

Apart from the effect of inadvertent activation of gangue minerals by copper sulphate Shackleton et al. (2007a and 2007b) have shown that there can be another unintended negative consequences resulting from the use of copper sulphate. In the case of the Platreef ore, in which tellurides account for between 30-40% of the platinum, the addition of copper sulphate reduced recoveries of the tellurides from >90% to about 50% (Fig. 4). Interestingly this was not observed in the case of Pd As<sub>2</sub>.

Nyabeze and McFadzean (2016) carried out a comprehensive study of the effect of copper sulphate on the froth behaviour and flotation kinetics of both a Merensky and a UG2 ore both using laboratory tests and plant investigations. It was shown that for the UG2 ore, froth stability decreased with addition of copper sulphate. This was attributed to the formation of hydrophobic copper-xanthate species, which have a destabilising effect in the sparsely mineralised UG2 froth. The results of the surveys on a UG2 concentrator conducted with and without the addition of copper sulphate supported the results of the laboratory tests. Entrainability was reduced upon addition of copper sulphate and this resulted in an improvement in grade and a slight decrease in recovery presumably due to a less stable froth.

Moimane et al. (2016) showed increasing ionic strength of the plant water had no apparent effects on the performance of the depressants. It was previously mentioned that one of the unintended negative effects of increased depressant dosages is to reduce the froth stability due to the reduced concentration of solid particles in the froth and that this can be compensated for by increasing frother dosage. Corin et al. (2011) have in fact shown that an increase in the ionic strength of the system resulted in an increase in froth stability, leading to increased mass pulls and water recoveries. The use of high dosages of

depressant reduced final nickel recoveries presumably by depressing gangue/pentlandite composite particles but the copper recoveries were not affected by the high depressant dosage.

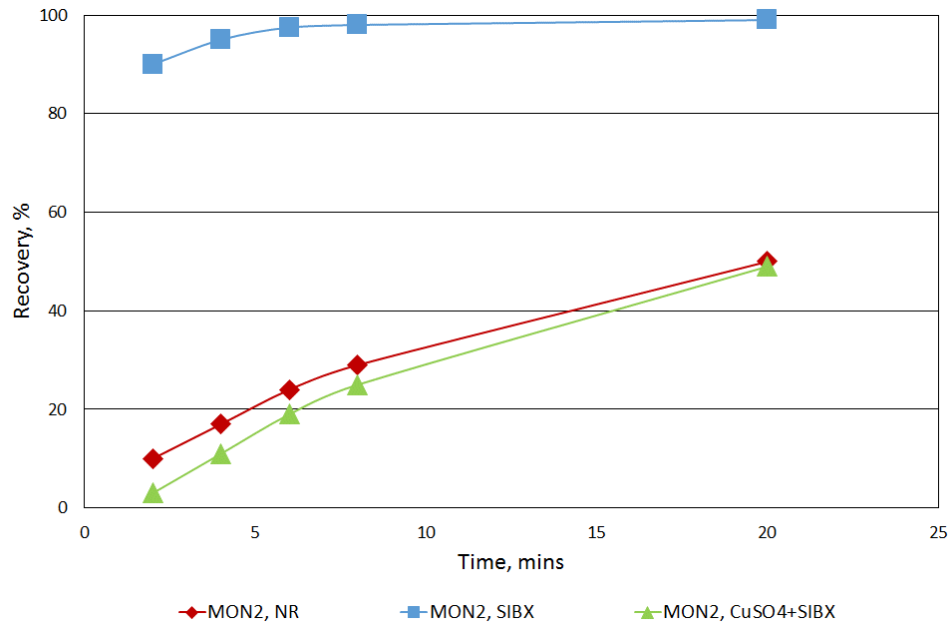


Fig. 4. Microflotation recovery - time plots for moncheite (PtTe<sub>2</sub>) using no reagent (NR), only SIBX and SIBX+CuSO<sub>4</sub> (Adapted from: Shackleton et al., 2007a)

### 3.5. Entrainment of gangue such as chromite

As shown above (Fig. 2) it is possible to completely depress the naturally floatable gangue by using depressants at dosages in excess of about 300g/t. However hydrophilic gangue will still report to the concentrate through entrainment. One of the most significant of those gangue minerals is chromite which, as already referred to, can constitute between 60-90% of the content by volume of the UG-2 ore. Chromite is of particular importance since when present in the concentrate at concentrations in excess of about 5% can have major negative effects on the downstream smelting process. Chromite has also been shown not to respond to depressants (Alvarez-Silva et al, 2014) although it has been observed that there are specific cases where UG2 ore has undergone alteration that has resulted in talc rimming of chromite grains and in such cases the chromite can be effectively depressed with suitable depressants (Hay and Roy, 2010). It is also possible to reduce chromite in the concentrate by prior use of gravity separation prior to secondary grinding (Maharaj et al., 2012). It is also well known that entrainment decreases with increasing particle size (Neethling and Cilliers, 2009) and hence fine grinding which is widely used in the processing of PGM ores will exacerbate the problem of managing chromite entrainment. Recently it has been observed that the entrainment of chromite is not only affected by the size and mass of the particles but also their shape with significant entrainment being observed for relatively coarse chromite particles with a high aspect ratio. These effects may have some important ramifications for the comminution procedures and devices currently used on concentrators (Wiese and O'Connor, 2016).

## 4. Conclusions

Depressants play a key role in the treatment of PGMs by flotation since they depress the recovery of the naturally floatable silicate gangue minerals which occur in abundance in all three major PGM-bearing ore bodies, viz. Merensky, UG2 and Platreef. Depressants also represent a very significant component of the cost of the reagents used in the flotation of PGMs. This paper has reviewed an extensive body of research carried out by the authors over an extended period investigating the role of depressants in the flotation of these ores. It has been shown that various polysaccharide depressants such as CMC and guar have different characteristics in terms of depressing the gangue minerals. These relate to the

different mechanisms whereby they adsorb onto the surface because of their different chemical structures and molecular weights. It has been shown that they do not affect the recovery of sulphides, which in the Merensky Reef, in particular, contain most of the PGEs. However, it was shown that copper sulphate, which is widely used as an activator in sulphide flotation, can inadvertently activate the gangue minerals and, in the case of the Platreef ore, reduce the recovery of PtTe<sub>2</sub> which accounts for up to 40% of the Pt in that ore body. Depressants also reduce the mass of solids reporting to the froth and can thus destabilize the froth. This effect on the froth can be mitigated by using higher frother dosages or water of higher ionic strength. In summary due care needs to be taken to carry out site test work to develop an optimum ratio of collector, frother, activator and depressant to ensure that the highest grades and recoveries of the PGEs are obtained while reducing depressant dosage as much as possible. It has also been shown that chromite generally does not respond to the use of depressants and given that it is a major gangue mineral needs to be removed using gravity separation and steps also taken to reduce entrainment through lower water recoveries.

### Acknowledgments

The authors wish to thank the following companies for their financial support: Impala Platinum, Anglo American, Lonmin.

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