Integrated MLA-QXRD Process Mineralogy for Reagent Selection and Flotation Performance Evaluation of PGMs in Chromite Tailings

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***Abstract*—**Flotation of platinum group minerals (PGMs) from UG2 slimes is usually optimised by trial and error. This study demonstrates the extent to which flotation performance can be predicted from feed mineralogy prior to flotation testing. A feed (22.3 g/t 4PGE) and its flotation concentrate (57.6 g/t) were characterised by Mineral Liberation Analysis (MLA) sparse-phase search, quantitative X-ray diffraction and fire assay. 354 and 523 PGM grains were measured. The feed PGMs were very fine (median 4.4 µm; 78 % of grains below 6 µm) and 36 % of the PGM volume was not conventional PGE sulphide but laurite, bismuthotelluride, sulpharsenide, alloy or arsenide. The floatability index classed 70 % of the PGM as fast-floating, 26 % as slow-floating and 4 % as non-floating. Liberation depended strongly on host particle size: 84 % of the PGM in the −25 µm fraction was liberated against 14 % in the +25 µm fraction, which held 17 of the 19 locked grains. The concentrate confirmed five of six feed-based predictions: liberated PGM rose from 66 % to 79 %, locked PGM fell from 3.9 % to 0.2 %, fast-floating PGM rose to 84 %, and chromite and Mg-silicate alteration minerals diluted the concentrate. Non-sulphide PGMs, expected to float less well, were concentrated at least as well as the sulphides. Feed MLA thus identifies the grind, collector, depressant and residence-time decisions before test work begins, but speciation response must be verified for each reagent scheme.

***Index Terms*—**Flotation, grain size, mineral liberation analysis, platinum group minerals, process mineralogy, UG2 chromite

I. Introduction

The Bushveld Complex of South Africa hosts most of the world's platinum group element (PGE) resources, and the UG2 chromitite reef has become one of its principal sources of PGE feed. Decades of mining have also left large stockpiles of historical UG2 chromite residues and flotation tailings that still carry PGEs. As run-of-mine grades fall, these residues are increasingly seen as a secondary resource that adds value from material already mined and processed [1], [2]. Re-treatment, however, has so far delivered modest gains: industrial tailings scavenging typically adds only 1–2 % to the recovery of the primary plant, equivalent to roughly 12–30 % PGE recovery from the re-treatment feed [2].

Several mineralogical factors make UG2 material difficult to float. The PGMs are fine and often only partly liberated, and the residues that resisted primary flotation are, by definition, the more difficult fraction [2]. Chromite, abundant in UG2, reports to the concentrate largely by entrainment, particularly when the ore is over-ground, and must be held below smelter limits [3]. Silicate gangue such as orthopyroxene and plagioclase can carry talc coatings that make it naturally floatable, so polysaccharide depressants such as carboxymethyl cellulose (CMC) and guar are needed to protect concentrate grade [4], [5]. Each of these problems has a mineralogical cause that can, in principle, be measured before flotation.

The PGM assemblage itself is a further variable. PGE sulphides closely associated with base-metal sulphides (BMS) are generally regarded as the readily floatable part of the PGM population, but UG2 and related ores also contain laurite, alloys, sulpharsenides, arsenides and bismuthotellurides in proportions that vary with hydrothermal alteration [6]. Rose et al. [6] showed that the bulk Pt/Pd ratio, a proxy for alteration, may help predict plant performance on UG2 and Merensky ore. For the Platreef, where Pt and Pd tellurides and arsenides make up about half of the PGMs and some report to the tailings, O'Connor and Shackleton [7] found that a xanthate collector raised the recovery of all the Pt and Pd minerals they tested, whereas copper sulphate activation lowered it. Reagent choices that suit a sulphide-dominated assemblage may therefore be inappropriate for a feed rich in other species.

Automated mineralogy can quantify all of these factors on the same sample. Mineral Liberation Analysis (MLA) identifies each mineral and PGM grain, measures its size, and records whether it is liberated and what it is attached to [8]. Mintek's floatability index combines PGM and BMS size, liberation and association into fast-floating, slow-floating and non-floating classes [9], and integrated mineralogical and flotation studies have been used to manage gangue in PGM circuits [10]. In practice, however, such data are usually collected after flotation test work, to explain results that were obtained by varying grinds and reagents by trial.

Fewer studies ask the reverse question: how much of the flotation outcome can be read from the feed mineralogy before any test, and how well do the products confirm those predictions? For historical UG2 chromite, three aspects are rarely reported together: full PGM grain-size statistics by species and mode of occurrence; the dependence of PGM liberation on host particle size; and the composition of the tailings, which is often not analysed.

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This paper addresses that gap using a UG2 slimes feed and its flotation concentrate. Its aims were (i) to characterise the feed PGMs in detail, including speciation, grain-size statistics, mode of occurrence by host-particle size, associations and floatability index; (ii) to derive flotation predictions from the feed alone and test them against the concentrate; (iii) to calculate the tailings composition by mineralogical mass balance; and (iv) to translate the results into a sequence of flotation decisions that can be made before test work begins.

II. Materials and Methods

A. Samples and Assays

A representative feed sample of UG2 slimes and the concentrate from its flotation test were submitted to for PGE grades they were determined by 4PGE fire assay with nickel sulphide collection and ICP-OES finish (detection limit 0.1 ppm). Bulk mineralogy was determined by quantitative X-ray diffraction (QXRD) on a Bruker D8 Advance (Co Kα, 5–80° 2θ), with Rietveld quantification in TOPAS.

B. Mineral Liberation Analysis

Each sample was rotary-split and screened into −25 µm and +25 µm fractions, which were mounted as 30 mm polished sections and analysed on an FEI 650F MLA in sparse-phase dual-zoom (SPL-DZ) mode. This bright-phase search locates PGM grains by their high backscattered-electron intensity and maps the particle in which each grain occurs. Grain size is reported as equivalent circle diameter (ECD). PGM abundances are reported as vol%, derived from measured grain areas. Large grains were not removed, so all grain-size data carry a nugget effect.

PGM grains were classed by mode of occurrence (Fig. 1): liberated (L); with liberated base-metal sulphide (BMS) (SL); attached to silicate or oxide gangue (AG); with BMS attached to gangue (SAG); with BMS locked in gangue (SG); and locked in gangue (G). Mintek's floatability index [5] then classes PGM as fast-floating (liberated PGM > 3 µm, or liberated BMS > 10 µm), slow-floating 1 (liberated grains below those sizes, or larger grains attached to gangue), slow-floating 2 (small grains attached to gangue), or non-floating (locked). Grain-size statistics for the feed were calculated from the individual grain records; those for the concentrate from the class distributions.

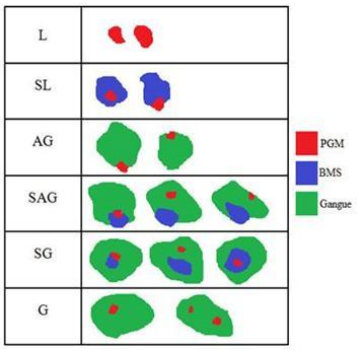


Fig. 1. Modes of occurrence of PGM (red) with BMS (blue) and gangue (green) [11].

III. Results

A. Grade and Bulk Mineralogy

Flotation raised the grade from 22.3 to 57.6 g/t 4PGE, an enrichment ratio of 2.6 (Table I). Both samples are dominated by plagioclase, pyroxene and chromite. The concentrate holds less chromite and plagioclase than the feed but markedly more chlorite (2.1 to 7.9 %), lizardite (2.8 to 7.5 %) and talc (< 1 to 2.2 %), the Mg-silicate alteration minerals that float naturally or as slimes[10],.

TABLE I: Grade and Bulk Mineralogy (QXRD, mass %)

	Feed	Concentrate
4PGE grade (g/t)	22.27	57.56
Plagioclase	33.9	29.6
Pyroxene	25.6	27.7
Chromite	20.0	16.0
Mica	7.3	3.9
Hornblende	4.0	3.2
Quartz	2.9	1.7
Lizardite	2.8	7.5
Chlorite	2.1	7.9
Talc	< 1	2.2
Pyrrhotite	< 1	< 1

B. PGM Speciation

Nineteen PGM species were identified in the feed and 22 in the concentrate, in six groups (Table II, Fig. 2). PGE sulphides dominate both: in the feed, PtRhCuS (26.6 %) and Pt–Pd–Ni sulphide (23.7 %) together make up half of the PGM volume. The other 36 % of the feed PGM is less conventional: laurite (RuS, 11.8 %), bismuthotellurides (9.1 %), sulpharsenides (6.7 %), alloys (4.7 %) and arsenides (3.8 %). In the concentrate, the sulphide share fell to 55.5 % while laurite, bismuthotellurides, alloys and arsenides all rose.

TABLE II: PGM Species in the Feed and Concentrate

PGM	Feed vol%	Feed grains	Feed mean ECD (µm)	Conc. vol%	Conc. grains
PtRhCuS	26.6	72	5.2	15	77
PtPdS(Ni)	23.7	84	4.8	17	105
PtS	5.4	25	4.3	10	53
PtPdS	5.2	13	5.9	10	23
PdS	2.9	5	7.6	3	12
PGE sulphides	**63.9**	**199**		**55.5**	**270**
Laurite (RuS)	**11.8**	**42**	5.0	**13.2**	**59**
PdBiTe	4.6	21	4.4	9	54
PtPdBiTe	3.0	17	3.7	1	12
PtBiTe	1.5	9	4.0	2	20
Bismuthotellurides	**9.1**	**47**		**11.9**	**86**
PtPdAsS	3.4	11	5.2	3	19
PtAsS	2.7	21	3.5	2	15
PtRhAsS	0.6	8	2.8	2	9
Sulpharsenides	**6.7**	**40**		**6.5**	**43**
PtPdSn	3.0	12	4.7	1	10
PdPb	0.9	3	5.3	1	10
PtFe	0.4	3	3.7	3	19
PdHg	0.4	2	4.6	1	3
PdSb, PdGe	–	–		1	7
Alloys	**4.7**	**20**		**7.9**	**49**
PtAs	2.7	2	9.4	1	3
PtPdAs	0.6	2	5.8	2	1
PdAs, PtHgAs	0.5	2	4.6	2	12
Arsenides	**3.8**	**6**		**5.0**	**16**
Total	**100**	**354**		**100**	**523**

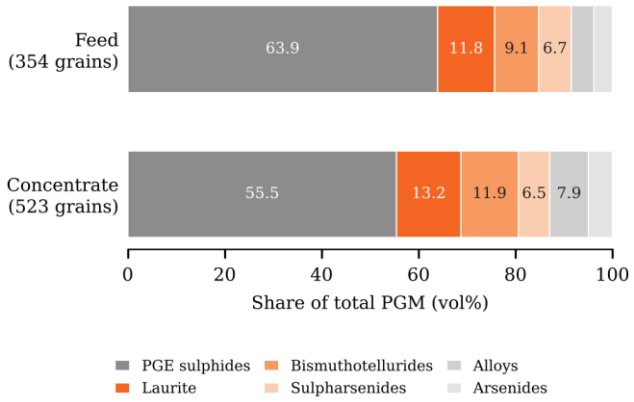


Fig. 2. PGM group distribution in the feed and concentrate.

C. *PGM Grain Size*

The PGMs are very fine (Table III). The median grain is 4.4 µm, 78 % of grains are finer than 6 µm and 28 % finer than 3 µm; the largest is 18.1 µm. Volume, however, is carried by the coarser grains: the volume-weighted median is 6.9 µm, and five grains of 15–21 µm hold 13 % of the PGM volume. Sulpharsenides (median 3.2 µm; 45 % below 3 µm) and bismuthotellurides (3.7 µm; 36 %) are the finest groups, laurite the most uniformly sized (only 10 % below 3 µm).

PGM grains in SL and SAG particles are finer (medians 3.6 and 3.2 µm; 42–46 % below 3 µm) than liberated grains (4.6 µm; 21 %). The finest PGMs therefore depend most on their BMS host. The concentrate has a similar number distribution to the feed (median about 4.5 µm) but a finer volume distribution: 77 % of its PGM volume lies below 9 µm against 67 % in the feed (Table IV, Figs. 3 and 4), because fewer coarse grains reached it.

TABLE III: PGM GRAIN-SIZE STATISTICS (ECD IN MICROMETRES)

Population	n	Mean	D10	D50	D90	Max	< 3 µm (%)
Feed, all grains	354	4.8	2.1	4.4	7.8	18.1	28
PGE sulphides	199	5.0	2.1	4.6	8.5	18.1	26
Laurite	42	5.0	3.2	4.6	7.6	13.6	10
Bismuthotellurides	47	4.1	1.8	3.7	6.5	9.7	36
Sulpharsenides	40	3.8	2.3	3.2	5.7	9.6	45
Alloys	20	4.6	2.3	4.2	7.7	8.0	25
Arsenides	6	6.6	2.4	5.8	11.7	16.8	33
Mode L	219	5.0	2.4	4.6	7.9	15.8	21
Mode SL	43	3.8	1.9	3.6	5.8	7.7	42
Mode AG	18	6.3	2.8	5.4	10.0	16.8	11
Mode SAG	54	4.2	2.0	3.2	6.9	18.1	46
Mode G	19	4.2	2.3	3.7	5.9	11.2	32
−25 µm fraction	265	4.8	2.3	4.4	7.8	16.0	26
+25 µm fraction	89	4.7	2.0	4.0	7.5	18.1	31
Feed, class data*	354	–	–	4.3	8.3	18.1	28
Conc., class data*	523	–	–	4.5	8.3	19.6	25

*D50 and D90 interpolated from the size classes in Table IV, for like-for-like comparison of feed and concentrate. Statistics are number-based; the SG class (one grain, 6.8 µm) is omitted.

TABLE IV: PGM GRAIN-SIZE DISTRIBUTION BY CLASS

ECD class (µm)	Feed num%	Conc. num%	Feed vol%	Conc. vol%
0–3	27.7	25.2	5.0	4.0
3–6	50.6	48.4	35.0	33.6
6–9	15.3	21.6	26.5	39.6
9–12	4.2	3.6	15.4	12.7
12–15	0.8	0.4	5.3	2.0
15–18	1.1	0.4	9.7	3.3
18–21	0.3	0.4	3.1	4.8
21–24	–	–	0.5	–

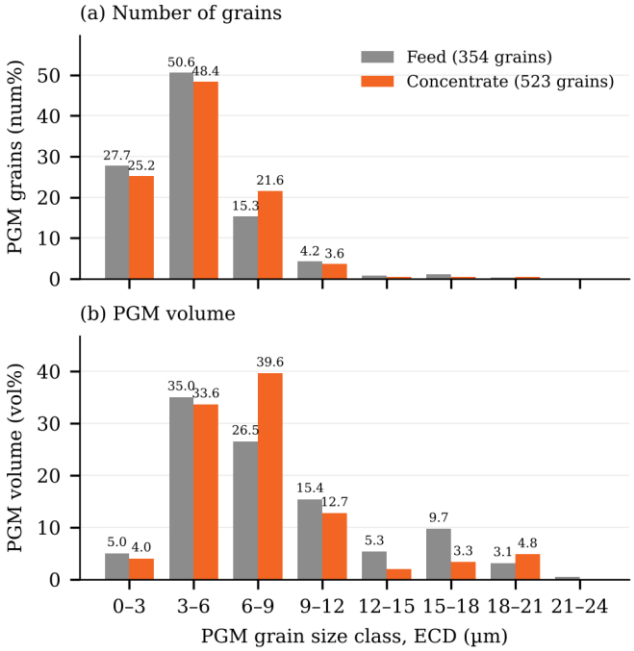


Fig. 3. PGM grain-size distribution of the feed and concentrate by size class: (a) number of grains; (b) PGM volume.

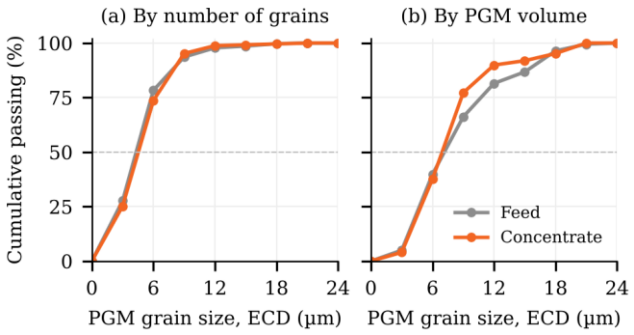


Fig. 4. Cumulative PGM grain-size distributions of the feed and concentrate.

D. *Mode of Occurrence, Host Particle Size and Floatability*

In the feed, 65.7 % of the PGM volume is liberated and 6.9 % sits on liberated BMS; 23.0 % is attached to gangue (AG 8.8 %, SAG 14.2 %) and 4.3 % is locked (G 3.9 %, SG 0.4 %). Liberation depends strongly on host particle size (Fig. 5, Table V). In the −25 µm fraction, 84 % of the PGM volume is liberated and only 0.4 % locked. In the +25 µm fraction, only 14 % is liberated, 56 % is attached to gangue, and 14 % is locked; this fraction holds 17 of the 19 locked grains and 36 of the 54 SAG grains. By liberation, laurite (85 % liberated by volume), sulpharsenides (85 %) and alloys (79 %) are better liberated than the PGE sulphides (65 %) and bismuthotellurides

(40 %).

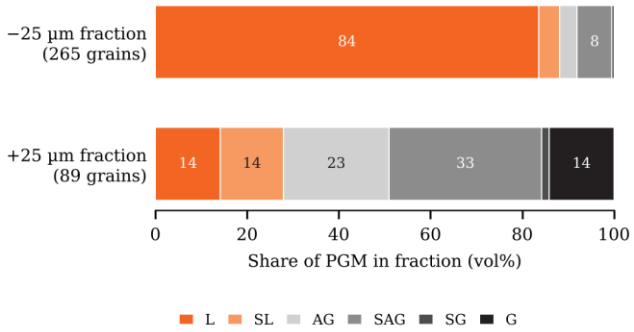


Fig. 5. Mode of occurrence of feed PGM in the −25 µm and +25 µm fractions.

TABLE V: MODE OF OCCURRENCE OF PGM (VOL%; GRAIN COUNTS IN BRACKETS)

Mode	Feed −25 µm	Feed +25 µm	Feed total	Conc. total
L	83.6 (213)	14.2 (6)	65.7 (219)	79.5
SL	4.5 (26)	13.7 (17)	6.9 (43)	8.9
AG	3.9 (6)	23.1 (12)	8.8 (18)	7.0
SAG	7.6 (18)	33.2 (36)	14.2 (54)	4.5
SG	0 (0)	1.7 (1)	0.4 (1)	0.0
G	0.4 (2)	14.1 (17)	3.9 (19)	0.2
Share of feed PGM	74.2	25.8	100	–

Among grains finer than 3 µm, only 17.4 % of the feed PGM volume is liberated; 43.2 % sits on liberated BMS and 19.7 % in SAG particles. In the concentrate, 48.0 % of the < 3 µm PGM volume is liberated. The floatability index classes 69.7 % of the feed PGM as fast-floating, 21.8 % as slow-floating 1, 4.2 % as slow-floating 2 and 4.3 % as non-floating; in the concentrate the fast-floating share is 84 % (Fig. 6).

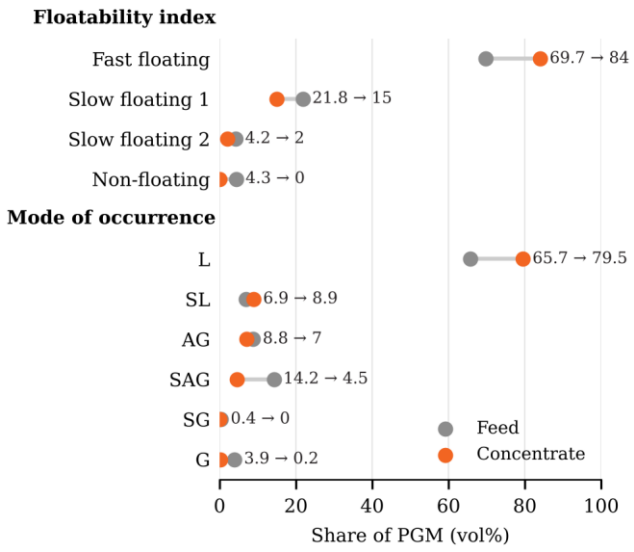


Fig. 6. PGM floatability index and mode of occurrence in the feed and concentrate.

E. *PGM Associations*

Plagioclase is the dominant gangue partner of non-liberated PGM in both samples (Table VI), followed by hornblende and enstatite. PGM attached to chromite rose from 3 grains in the feed to 13 in the concentrate, and PGM attached to enstatite from 8 to 15. Pentlandite is the main BMS host, carrying 66 of the 98 BMS-associated PGM grains in the feed, followed by chalcopyrite (16) and pyrite (8). BSE images of typical occurrences are shown in Fig. 7.

TABLE VI: GANGUE AND BMS PARTNERS OF NON-LIBERATED PGM (GRAIN COUNTS)

Partner mineral	Feed	Concentrate
Plagioclase	44	39
Enstatite	8	15
Chromite	3	13
Hornblende	12	12
Titanite	1	7
Diopside	5	6
Chlorite	5	3
Quartz	5	1
Other (rutile, apatite, monazite, mica, unknown)	9	4
Total gangue-associated	**92**	**100**
Pentlandite	66	103
Chalcopyrite	16	20
Pyrite	8	9
Pyrrhotite	6	2
Galena	2	1

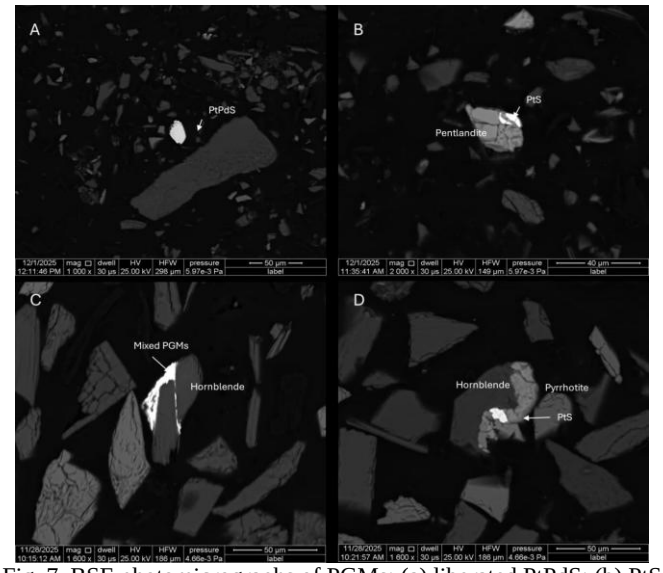


Fig. 7. BSE photomicrographs of PGMs: (a) liberated PtPdS; (b) PtS attached to pentlandite; (c) mixed PGMs attached to hornblende; (d) PtS at a pyrrhotite–hornblende contact.

IV. DISCUSSION

A. *What the Feed Predicted and the Concentrate Confirmed*

Six predictions can be drawn from the feed mineralogy before any flotation test (Table VII). Five were confirmed by the concentrate. The rougher should recover the fast-floating PGM, about 70 %; the concentrate is 84 % fast-floating and the grade rose 2.6-fold. Locked PGM should stay behind, and G fell from 3.9 % to 0.2 %. SAG PGM should float slowly, and SAG fell from 14.2 % to 4.5 %. Fine PGM should depend on its BMS host, and pentlandite remained the main host. The Mg-silicate alteration minerals and chromite should dilute the concentrate, and they did.

TABLE VII: FEED-BASED PREDICTIONS TESTED AGAINST THE CONCENTRATE

Prediction from feed MLA	Concentrate result	Verdict
About 70 % of PGM floats fast (index 69.7 %)	Fast-floating 84 %; liberated 79.5 %; grade 2.6×	Confirmed
Locked PGM stays behind (G 3.9 %, SG 0.4 %)	G 0.2 %, SG 0 %	Confirmed
SAG PGM floats slowly (14.2 %)	SAG 4.5 %	Confirmed
Fine PGM depends on BMS host (43 % of < 3 µm on liberated BMS)	48 % of < 3 µm liberated; pentlandite main host	Confirmed
Chromite and Mg-silicates dilute (chromite 20 %)	Chromite 16 %; chlorite 7.9 %; lizardite 7.5 %; talc 2.2 %	Confirmed
Non-sulphide PGM (36 %) floats less well	Non-sulphide share rose to 45 %	Not confirmed

The speciation result is the instructive exception. Bismuthotellurides and arsenides are often expected to respond poorly to xanthate [12], yet their share of the PGM rose in the concentrate, as did that of laurite and the alloys. Laurite, sulpharsenides and alloys were well liberated in the feed (79–85 %), which may explain their behaviour. The bismuthotellurides, however, were only 40 % liberated and still concentrated. Textbook rankings of species floatability are therefore an unreliable guide for this material, and speciation response has to be measured for each reagent scheme [13].

B. Why Know Your Feed

Each feed measurement points to a specific flotation decision. The host-size result matters most. Locked and gangue-attached PGM is concentrated in the +25 µm fraction, which carries a quarter of the feed PGM, so the grind, or a regrind of the scavenger concentrate, is the main lever for the 26 % slow-floating and 4 % non-floating PGM. The fine grain size calls for adequate residence time and fine-particle conditions. The dependence of fine PGM on pentlandite points to BMS activation. The XRD alteration minerals call for a depressant such as CMC and for cleaner stages. A 36 % non-sulphide PGM population justifies screening a co-collector. All of these decisions can be made before the first flotation test, and the concentrate MLA then confirms them.

V. CONCLUSION

MLA of a UG2 slurry feed (22.3 g/t 4PGE) revealed an exceptionally fine PGM population, with a median grain size of 4.4 µm and 78% of grains smaller than 6 µm, as well as a significant proportion (36%) of non-sulphide PGMs. Based on mineralogical characteristics, 70 % of the PGM were classified as fast-floating, 26 % as slow-floating and 4 % as non-floating. Liberation was controlled by host particle size: 84 % liberated in the −25 µm fraction against 14 % in the +25 µm fraction, where nearly all locked PGM occurred. The concentrate (57.6 g/t) confirmed five of six feed-based predictions, including the liberation gain, the rejection of locked and gangue-attached PGM, and dilution by chromite and Mg-silicate alteration minerals. Contrary to expectations, non-sulphide PGMs reported to the concentrate at least as effectively as the conventional PGE sulphides, highlighting the importance of verifying mineral-species behaviour for a given reagent regime. Feed mineralogy therefore identifies the grind, collector, depressant and residence-time decisions before test work begins. MLA of the tailings is the next step, to turn compositional shifts into recoveries by species and mode.

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