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The valorisation of platinum group metals from flotation tailings: A review of challenges and opportunities

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ABSTRACT

Flotation tailings from South Africa's platinum group minerals (PGM) represent complex polymetallic orebodies comprising a low-grade platinum group elements (PGE) content and complex mineralogical composition. Nevertheless, given the valuable mineral potential in the tailings, it is understandable that the substantial historic tailings deposits and sizeable annual production volume from primary processes represent a potential secondary resource. For several decades, valorising the PGM tailing materials received very little interest due to limitations associated with extractive metallurgical technology to achieve economically viable PGE extraction. The early 21st century saw the coming online of technologies, including but not limited to ultrafine grinding, suitable to meet challenges in primary metallurgical treatment processes to recover valuable minerals from ultrafine particle fractions, which could not otherwise be recovered. More so, such processes were critical in improving the liberation of partially liberated particles without compromising additional ultrafine generation. These technologies led to the development of re-treatment pilot tests and subsequent industrial re-treatment recovery processes. The current industrial re-treatment approach – via tertiary scavenging flotation circuits – renders profit in small increments up to 1 ~ 2% additional recovery relative to the primary plant head grade. These small increments relate to about ~12–30% PGE recovery of the feed grade to the re-treatment circuit, thereby enhancing the primary plant's overall economics as well as aiding the supply of critical metals to meet global demands. With a focus on South Africa, this review provides an overview of (a) the current and future drivers of the precious metals global demand; (b) proffers discussion on the PGM characteristic mineralogy and the metallurgical value chain; (c) relates the parent orebodies ("reefs") mineral characteristics to the inherent processed tailings; (d) estimates the economic potential these massive processed waste materials contain, (e) provides an overview of existing technologies that are industrially used in tailing re-treatment plants; and (f) outlines a comprehensive understanding of the nature of value minerals rejection to tailings.

1. Introduction

The global demand for platinum group elements (PGE) continues to rise. This increase in demand is motivated by the drive toward green transition minerals and metals, primarily for industrial applications as emission control catalysts in the automotive industry, chemical and petrochemical refineries, fuel cell technology, dental and medical equipment, alloy fabrication, wear resistance, high-temperature and electronic sectors as well as in jewellery, glassmaking, and investments (Glaister and Mudd, 2010; USGS, 2021; Johnson Matthey, 2021, 2022). The annual global production of the platinum group minerals (PGM) rose yearly from approximately 400 t to about 635 t between 2016 and 2018 (Blengini et al., 2020). However, the Covid-19 pandemic caused severe disruptions to major producers, with outages resulting in a ~ 16%

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decline in the combined global PGM supplies in 2020 (Johnson Matthey 2021). More so, some of the major concerns for a sustainable PGE supply to the global economy include, *inter alia*, recurring rise in government tariffs on electricity in the South African scenario (i.e., the world's leading platinum-producing country), lower grade of the *in-situ* and plant feed ore, coupled with complex mineralogy, ensuing high processing costs, and more stringent policy measures from governments on producing companies (Safarzadeh et al., 2018; Blengini et al., 2020; Corin et al., 2021).

The platinum group elements - platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os) - are a group of six elements that occur together in nature with gold, silver, and base metals – predominantly nickel and copper. These elements are found in a host of different minerals, which together are called platinum group minerals (PGMs). The group of metals has very similar chemical properties, while their physical properties vary slightly. The PGEs' unique characteristics have found significant application in the global economy. Due to the high industrial importance, limited geographic minable reserves, unique properties, and noble application resilience, the mineral group is labelled among the "critical raw materials" in the global economy (Thormann et al., 2017; USGS, 2019, 2023; European Commission, 2020, 2023; Bao, 2020). The most commercially viable metals of the PGEs are in the order of platinum, palladium, and rhodium (Hay and Roy, 2010; Johnson Matthey, 2021).

The acronyms PGM and PGE represent platinum group minerals and platinum group elements, respectively: where the PGMs are minerals - sulfides (PtS), arsenides ($PtAs_2$), etc - containing the elements/metals – PGEs: Pt, Pd, Rh, Ru, Ir and Os. Some researchers may refer to the elements (PGEs) as metals– i.e. platinum group metals (PGMs); such naming description, however, is author dependent. For this contribution, PGM and PGE are used to indicate platinum group *minerals* and platinum group *elements* (i.e. metals), respectively. In industrial practice, the relevant PGE metal grade may also be referred to in short as 2E (Pt, Pd), 3E (Pt, Pd, Au), 4E (Pt, Pd, Rh, Au), or 6E (Pt, Pd, Rh, Ir, Ru/Os, Au).

1.1. Global platinum group mineral resource distribution

Mineable PGM-bearing ore deposits are concentrated in enriched mafic and ultramafic magma intrusions representing host lithology from igneous origins (Haldar, 2017). The mineral group occurs in sulfide and peridotite where the sulfides are the most common carriers responsible for PGE distribution and concentrations in the melt (Naldrett and Duke, 1980; Mudd et al., 2018). Major mineral associations of the PGEs are in base-metal sulfides, bonded in compounds forming mineral alloys of sulfides, arsenides, antimonides, tellurides, and a host of other less common PGM-bearing minerals (McCutcheon, 2013; Smith, 2013; Mwase, 2016; Rose, 2016; Molifie, 2021). Global PGE resources are constrained by geographic distribution and a limited number of economically mineable mineral reserves are concentrated in only a few countries: Fig. 1 shows major PGE primary producers. Extractable PGM deposits are located in the Bushveld Igneous Complex (BIC) in South Africa, the Great Dyke in Zimbabwe, the Noril'sk–Talnakh in Siberia (Russia), the Sudbury and Lac Des Iles Igneous Complexes in Canada, and the Stillwater Igneous Complex in the United States. Other PGE minor occurrences are in Kambalda Western Australia, Kola Peninsula in Russia, Northern Finland, and Jinchuan in China (Gunn 2014; Arctic Platinum 2019; Blengini et al., 2020).

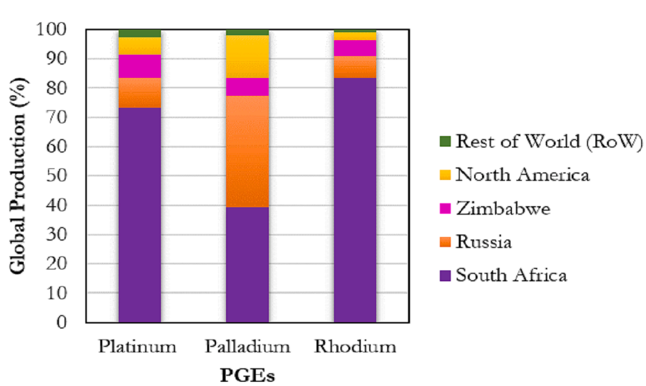

Fig. 1. Platinum group element global producing countries data adopted from Johnson Matthey 2021.

The BIC is the largest known repository of PGE global resources, primarily in the Upper Group 2 (UG2), Merensky Reef, Platreef, and the BIC satellite intrusion, Nkomati Nickel Deposit (Blengini et al., 2020; USGS 2022). South Africa remains the world's top producer of platinum and the second-largest producer of palladium (McFadzean et al., 2015; Johnson Matthey 2019). South Africa alone holds about ~ 90% of the world's estimated known resource, and is the primary contributor of 80% of the global production of Platinum (Pt) and Palladium (Pd) (Sinisalo and Lundström 2018; Bao 2020; USGS 2021–2023). The Main Sulfide Zone (MSZ) hosted in the layered intrusion Great Dyke in Zimbabwe contains the second-largest reserve of PGE worldwide (Thormann et al., 2017). The Noril'sk-Talnakh deposit in the Taimyr Peninsula, Siberia (Russia) is mined primarily for nickel-copper dominant ores and produces PGM as a by-product. Russia's Noril'sk is the largest producer of palladium and holds a significant rank in the global platinum supply (Nornickel 2018, 2020). Like Russia, the North American PGM deposits contain a high proportion of palladium (IPA 2020). The main global supply of rhodium, ruthenium, and iridium emanates from South Africa followed by marginal supplies from Russia and Zimbabwe (Thormann et al., 2017; Blengini et al., 2020; Johnson Matthey; 2021).

The commercial grade of PGM primary resources are low, typically in the range 1 – 10 g/t 6E in South Africa, Russia, and Zimbabwe (Crundwell et al., 2011; Zientek et al., 2017). The average processed head grade between 2010 and 2015 for the Southern African ore bodies was 3.58 g/t 6E and 3.40 g/t 4E (Thormann et al., 2017) and has remained in the range 3 – 5 g/t for both 4E and 6E over the decade. Russia's Nornickel ore reserve (from Taimyr and Kola Peninsulas) over the last decade reported grade averages at ~ 4.73 g/t 3E and ~ 4.75 g/t 6E. It should be reiterated that a significant portion of Nornickel ore reserve is contained in the Taimyr Peninsula with average grade reported at ~ 5.97 g/t 3E and ~ 6.0 g/t 6E for the same period (Nornickel 2010-2020). The Northern America PGM mineralisations contain varying ranges about ~ 3.0 g/t 3E for Canada and 7.0 – 40.0 g/t 2E for the United States (Impala AR 2020; Sibanye Stillwater AR 2020). Table 1 summarises the average mineral resource and reserve estimate from major producing countries - reported for 2021.

1.2. Global platinum group mineral supply, demand, and outlook

1.2.1. Supply and challenges

South Africa currently accounts for the greater supply of PGEs - iridium (92%), platinum (71%), rhodium (80%), ruthenium (80%) – while Russia remains the major supplier of palladium (40%) followed by South Africa (37%), Canada (10%), US (6%), Zimbabwe (5%), and other countries (2%). (Blengini et al., 2020; Grohol and Veeh 2023). The year 2022 saw unusually widespread uncertainty as it relates to the PGM supply from Russia given the on-going Ukraine invasion. While Russia faced imposed sanctions by the West, Norilsk Nickel, Russia's PGM producer, recently reported (Nornickel 2023) that the company has not been sanctioned (as of the writing of this paper). However, according to a Johnson Matthey (2022) report, the delisting of Russian refineries from the London Platinum and Palladium Market (LPPM) is predicted to affect the metal deliveries to the market. This concerns the supply of platinum, palladium, and rhodium but not ruthenium and iridium - primarily supplied from South Africa and Zimbabwe. More than two-thirds of the EU and the USA palladium supply has been reportedly exported from Norilsk Nickel. Johnson Matthey (2022) forecast that the

Table 1
Mineral resource and reserve estimate average grade of main platinum group element producers – 2021.

Production (%)	Ore Body/ Region	Source	Resource Estimate^	Reserve Estimate
South Africa	Bushveld Igneous Complex (BIC)[a]	Upper Group 2 (UG2), Merensky Reef, Platreef, and the BIC satellite intrusion Nkomati Nickel Deposit	~ 4.09 g/t 4E	~ 3.21 g/t 4E
Russia+	Taimyr Peninsula (Siberia)[b]	Noril'sk-Talnakh Deposit	~ 4.55 g/t 3E	~ 4.47 g/t 3E
Zimbabwe	Great Dyke layered intrusion[c]	Main Sulfide Zone (MSZ)	~ 3.56 g/t 4E	~ 3.23 g/t 4E
North America+*	Canada: Sudbury and Lac Des Iles Igneous Complexes[d] United States: Stillwater Igneous Complex[e]	Canada: Lac Des Iles intrusive complexUnited States: J-M Reef (Banded series)	~ 2.48 g/t 3E ~ 13.11 g/t 2E	~ 2.29 g/t 3E ~ 12.43 g/t 2E

+Produces platinum group elements as by-products. * North America: Canada and the United States. ^ Resource Estimate: includes measured, indicated and inferred data. (Gunn 2014; Thormann et al., 2017; Anglo platinum RR 2021[a]; Sibanye Stillwater RR 2021[a,e]; African Rainbow Minerals RR, 2010 - 2021[a]; Impala RR 2021[a,c,d]; Nornickel 2021[b]; Blengini et al., 2020; Northam RR 2021[a]).

LPPM delisting of Norilsk Nickel is expected to change the trends of supply to Western consumers in the short future. This should inherently increase the metal market demand on the primary Southern African suppliers and secondary (recycling and tailing re-treatment) producers. The source of PGM supply from the South African producers is suggested to not be an issue considering the massive reserve distribution South Africa owns and its annual production, coupled with supplies from recycling. Nevertheless, prominent among the concerns about the security of PGM supplies from South Africa that affect the PGM industry are socio-economic factors: including strike actions leading to disruptions of operations (fuelled by labour wage negotiations), interrupted power supplies (national 'load shedding' schedules), and community unrest to name a few (Blengini et al., 2020; USGS 2022; Johnson Matthey 2022). Important to acknowledge is the impact the Covid-19 pandemic also unavoidably had on the global PGM demand, which severely hindered primary production; however, although still very volatile, most PGE markets are recovering to pre-Covid trends (Johnson Matthey 2022).

1.2.2. Demand, applications, and prospects

The PGEs' distinct applications drive their global demand in many industrial sectors. The future for green hydrogen toward net-zero emission is shifting global interest to grasp the opportunities that PGM offer for applications in clean energy technology. Hydrogen is seen as a keen player to serve the global energy demand in efforts toward decarbonation. The drive for clean hydrogen with the aim to achieve net-zero is to have its production emitting very minimal CO_2 as much as possible to be considered "green" (Johnson Matthey 2021). The EU, UK, China, Japan, and USA are major actors leading implementations toward the net-zero policy through various stages of regulations that are shaping industrial manufacturers as well as research and development in all sectors toward achieving the green economy strategy. This has led to stringent regulations for emission control systems in motor vehicles production – i.e. PGE demand for catalyst manufacture in the automotive industry (Blengini et al., 2020). Along with the automotive industry, industrial catalyst production for chemical and petroleum refining, as well as the growing interest and application of fuel cell technology significantly contribute to the global demand for current applications. Europe is ranked as the largest regional consumer of platinum in the autocatalytic industry. At the same time, the Chinese economy is expected to boost the noble metals demand in autocatalyst production (for trucks and gasoline automotive), glassmaking, and jewellery fabrication industries (Johnson Matthey 2021). Catalytic converter manufacture is predicted to substantially drive PGM demand given the increasing sales for both light-duty and heavy-duty vehicles and stricter emission standards (IPA 2019). However, growing interest in the development of battery electric vehicles is viewed to eventually make obsolete the global demand for PGE, where internal combustion engines are anticipated to progressively be replaced by electric vehicles – requiring no catalytic converter (Blengini et al., 2020). Notwithstanding, fuel cell technology – with the application of platinum catalyst in fuel cell electric vehicle – is expected to serve a cardinal role in decarbonating the transportation sector to cleaner forms (Johnson Matthey 2018, 2021). Despite automakers shifting production focus into battery electric vehicles in response to regulations and consumer demand for net-zero emission vehicles to achieve carbon emissions targets, fuel cell electric vehicles will eventually outperform battery electric vehicles, thereby promising continuous growth of PGE demand in the future hydrogen-automotive fleet and non-automotive fuel cell systems (Heraeus 2019; Blengini et al., 2020; Johnson Matthey 2021, 2022).

PGE application in fuel cell electric vehicles (compared to battery electric vehicles) as well as electrocatalyst in proton exchange membrane (PEM) clean energy technologies – i.e. fuel cell catalyst-coated membrane and PEM electrolyser catalyst-coated membrane for direct hydrogen production – are forecast to be the major drivers of PGE demand in the long-term future hydrogen economy (European Commission, 2020; Johnson Matthey, 2021). The performance of PGEs in PEM electrolysis is superb and unparalleled by any alternative materials. Unlike the automotive industry (i.e. in gasoline emission systems), where catalyst loadings can be reduced and substitution with platinum (i.e. platinum-for-palladium or platinum-for-rhodium) are acceptable without compromising performance, iridium and ruthenium are yet to have any technically viable alternatives in PEM electrolysis (USGS 2022; Johnson Matthey 2022). Reducing PGE (iridium and ruthenium) loadings to satisfy reduced capital cost compromises the lifetime, durability, and reliability of the electrolysis process hence resulting in increased operating cost. Considering the efficiency of PEM over the liquid alkaline electrolysis and solid-oxide electrolysis processes, PGE demand will continue to be high in the long-term. The global energy transition along with the role of PGEs in their application in automotive fuel cells is gradually gaining momentum, suggesting that a global noble metals boom for applications in the hydrogen economy is imminent.

Most importantly, PGE alloys in many applications can only be substituted by other PGEs, which still comes down to the fact that demand for PGE remains on the whole strong – prominently for platinum. The outlook of PGEs in existing and future applications promises persistent demand. Essentially, whichever way one views the current and future application of PGEs, the gross global demand is strong, encouraging production of the precious metal group through primary as well as secondary sources – i.e. recycling and tailing re-treatment processes.

1.3. Review rationale and objective

The global PGM supply from primary ores is complemented by production from secondary sources. Secondary sources are recycled materials from industrial and end-of-life products, as by-products from primary production residues of other commodities and PGM process tailings (IPA 2020; Johnson Matthey 2021). Production from recycled materials dominate the secondary supply of PGEs due to their relatively high grade and the availability of suitable recycling processes achieving recovery of up to 95%. The grade of PGEs in recycling material from end-of-life or spent industrial scraps are in the range of 100 – 2000 g/t, whereas primary ores hold 2 – 6 g/t 4E, and residue from flotation tailings are 0.4 – 1.2 g/t 4E (Nel et al., 2004; Glaister and Mudd 2010; IPA 2020; Eastplats 2021). Given the high grades and recovery yields of the PGEs, secondary supply from recycling contributes significantly to the global demand, although there has been a slight decline in recent years. In 2018, the supply of Pt, Pd, and Rh from recycling amounted to 173 t, equivalent to 29% of the global supply (Johnson Matthey 2019). In 2019 and 2020, on the other hand, recycling of PGEs from scrap contributed only about 116 t and 102 t (combined Pt and Pd) to the commodity supply (USGS 2020, 2021).

Conversely, the processing of PGM-bearing ores is challenged by its complex mineralogy and the inherently complex metallurgical operations that require numerous unit stages where value losses occur along the treatment steps (Crundwell et al., 2011). Most PGM losses in the processing circuit occur during comminution and concentration stages, where flotation recovery for high-grade ores is 85 – 88% (i.e. for highly optimised circuits) and < 70% for low-grade and oxidized/weathered ores (Jones 2005; Ramonotsi 2011; Ndlovu 2015; Sinisalo and Lundström 2018). Moreover, the processing of primary ores is characterised by high energy consumption associated with fine grinding and a large amount of waste produced from mass reduction. Even though optimisation processes at concentrators have essentially improved the recovery and grade of primary processes, typically around 15% of unrecovered value PGMs are rejected to flotation tailings, likely more in un-optimised circuits. Unlike industrial scrap and end-of-life products, tailings (i.e. tailings arising from ongoing operations as well as tailings reclaimed from historic deposits in dams) and waste rock stockpiles are unattractive for re-processing due to extremely low grades (<0. 5 – 0. 7% PGE) and the often complex polymetallic mineralisation.

Legacy tailings in the BIC contains average PGE grades around ~ 0.78 g/t 3E and ~ 0.81 g/t 4E (Muthavhine, 2017; Anglo Platinum AR 2020). At the same time, massive stockpiles of mineral waste rock contain PGE grades generally < 2 g/t 4E – considered too low for value recovery with conventional processes, however they represent as much as 28% of Pt value lost from open pit operations (Ndlovu 2015). With millions of tonnes of mineral waste stockpiles (~64 Mt) and tailing (~72.3 Mt) material produced from mining and processing annually, these waste materials still need to be considered as potential mineral resource.

To date, there has been limited work toward characterizing and re-treating PGM flotation tailings and waste rock in the literature. The large tonnage accumulation of these very low-grade materials – ongoing and legacy flotation tailings and run-of-mine (ROM) waste rocks - require alternative treatment methods capable of extracting PGEs from poorly liberated and chemically inert gangue. In this paper, we focus on low-grade ore and flotation tailings (i.e. tailing inclusive of tailings from operating plants as well as historic storage facilities) from the Bushveld Igneous Complex (South Africa) to review the latest developments in PGE mining waste valorisation.

1.4. Review structure

This study aims to provide an understanding of the processing of PGEs, from their origin through the conventional primary treatment to their value rejection to tailings, as well as of existing alternative techniques to valorise PGE flotation tailings. The review consists of seven sections. Information was gathered and synthesized from published papers and company reports to develop each of the different sections. The present introduction gives a background and global resource distribution of PGE. A global outlook on PGM demand and the inherent benefits offered by valorising tailings in the commodity supply is reviewed; it also highlights industrial necessities and resource potential of flotation waste streams. In section 2 and 3, we review the general characteristics of the BIC PGM-bearing ore bodies and the inherent value chain of the primary treatment route. Section 4 provides explanation of value losses along the flotation concentration stage and final rejection to the tailings. We then explore in section 5, existing tailing re-treatment and low-grade ore processing techniques where we highlight process routes and pre-treatment opportunities that may assist in the re-treatment of the critical metals. In section 6, we provide a critical analysis of plant production data of major PGE concentrators in South Africa. The generated PGE recovery data was used to evaluate the economic potential of residual value minerals in flotation waste streams, while the reserve base of deposits was used to provide an outlook on tailings production given the current primary treatment methods. The metallurgical performance reported in this review covers a period of the last 5 – 10 years, 2011 – 2021. Finally, in section 7 we conclude with a summary. A graphical presentation of the review structure is illustrated in Fig. 2.

2. Characteristics of the Bushveld Igneous complex ore bodies

The mainstream PGE mineral-bearing source in South Africa are the Merensky Reef, UG2 Reef, and Platreef of the BIC in three regions, namely Western, Eastern, and Northern Limbs (Fig. 3). The primary sulfides occurring in these ore bodies are pyrrhotite ($Fe_{1-x}S$), pentlandite ($(Fe,Ni)_9S_8$), chalcopyrite ($CuFeS_2$), and minor occurrence of pyrite (FeS_2). Distribution of the base-metal sulfides (BMS), Table 2, varies in the different horizons, and they are disseminated as interstitial phases to or within their host silicates (Jones 2005; Corin et al., 2021). The PGM are largely associated with the BMS in solid solutions and minimal occurrence with oxides and silicate minerals (Ramonotsi 2011; Chipise et al., 2021; Molifie 2021). The PGEs essentially occur as latent association - PGE hidden/invisible in the BMS crystal structure - or as discrete phases hosted in PGMs (Smith 2013; Rose 2016). The average PGM 4E grades are relatively low coupled with exceeding fine grained (<10 μm) average size. They show complex mineralisation, namely as PGE-sulfides, PGE-alloys, PGE-tellurides, PGE-arsenides, PGE-bismuthides, Au + Electrum, PGE-BMS, PGE-(sulf)-arsenides, PGE-bismuthotellurides, and other minor PGE mineralisations (Shamaila and O'Connor, 2008; Liddell and Adams 2012; Rule and Schouwstra 2012; Rose 2016; Corin et al., 2021). Not only restricted to South Africa, PGMs globally occur in porphyry ores in solid solutions as Pd and minor Pt tellurides, bismuthinides, arsenides, and antimonides but rarely as PGM-sulfides, with the PGM grains in the range 2 – 50 μm (Safarzadeh

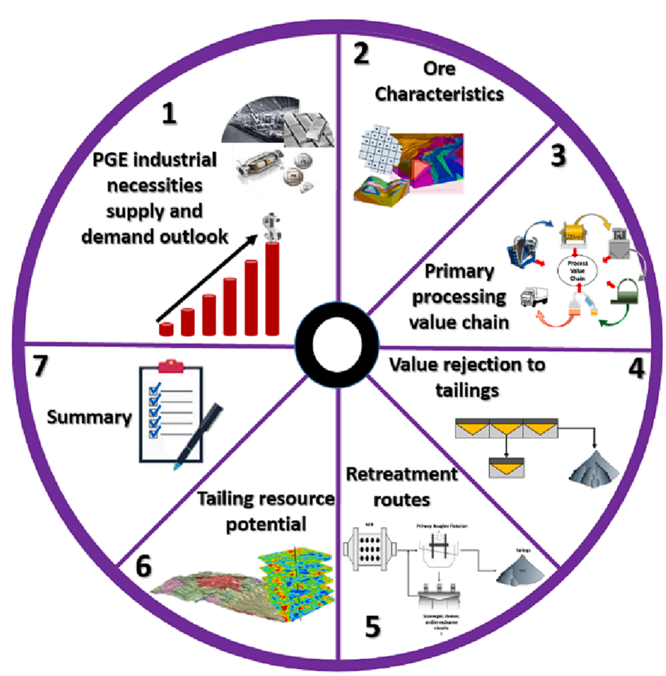

Fig. 2. Graphic illustration of the paper structure.

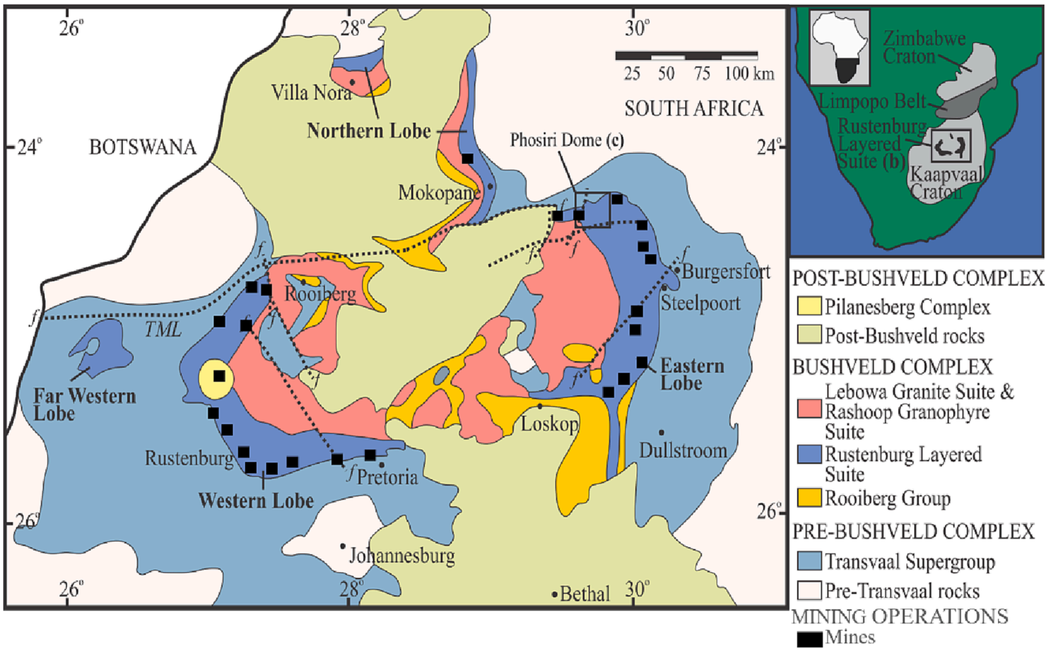

Fig. 3. Map of the Bushveld Igneous Complex showing the northern, western, and eastern limbs as well as mining operations; modified after Bourdeau et al. (2020).

Table 2
Base-metal sulfide modal mineral composition of Bushveld Igneous Complex ore bodies.

Ore Type	Base Metal Mineral Composition (%)				References
	Pentlandite ((Fe,Ni)$_9$S$_8$)	Chalcopyrite (CuFeS$_2$)	Pyrrhotite (Fe$_{1-x}$S)	Pyrite (FeS$_2$)	
Merensky	32	16	45	2–4	Jones 2005
	35	18	47	–	Kloppers et al., 2016
	28	14	51	7	Rose 2016
	26–32	17	50–54	1–2	Wiese et al., 2005
	39.7	19.9	26.5	13.2	Solomon et al., 2011
	29–39	19–23	38–52	–	Dzvinamurungu et al., 2013
	37	15	48	–	Smith et al., 2013
	43	14	36	7	Brough et al., 2010
	37	18	41	4	Lamya 2007
	35	20	46	–	Corin et al., 2021
	15–29	41–73	12–28	1–3	Molifie 2021
Platreef	38.6	18.2	40.9	2.2	Mwase et al., 2014
	27	19	52	–	Corin et al., 2021
UG2	35	10	50	–	Nel et al., 2005
	46	24	11	19	Rose 2016
	50	30	–	20	Becker et al., 2008
	44–52	21	26–35	–	Corin et al., 2021
	66	33	≪1	–	Dzvinamurungu et al., 2013

et al., 2018).

The chief gangue mineral association of the BIC platinum ores are pyroxene (orthopyroxene and clinopyroxene), chromite, and feldspar (plagioclase); while minor assemblages may include mica, quartz, serpentine, talc, tremolite, and traces of accessory minerals (Table 3 and Table 4). The host/gangue mineral assemblages of the primary BIC PGM-bearing reefs occur at different abundances suggesting different sub-facies in the individual ore bodies (Table 3). These variations in the modal abundances may be influenced by the sampling campaign, regions of the horizon, and/or mining cut investigated.

2.1. Merensky Reef ore body characteristics

Feldspathic pegmatoidal pyroxenite is the major rock type that characterises the Merensky Reef (Becker et al., 2013; Sahu et al., 2021). The predominant rock-forming mineralisation are orthopyroxene and plagioclase with minor appearances of clinopyroxene and chromite (Table 3); sporadically there are occurrences of phlogopite and olivine. Formation of secondary mineral assemblages exist, which include serpentine, chlorite, talc, and magnetite (Rose 2016; Corin et al., 2021). In regions of intense alteration in the "normal" pyroxenite unit, chalcopyrite is replaced by calcite and magnetite and the major silicates show alteration of plagioclase to serpentine as well as orthopyroxene to talc (Viti et al., 2005; Becker et al., 2013; Rose 2016). The BMS composition - in the order of decreasing abundance: pyrrhotite, pentlandite, and chalcopyrite - may vary between 0.25 and 1.6 wt% (average ∼ 1 wt%); and may occur in trace amounts as pyrite, troilite, and millerite (Bulatovic, 2003; Becker 2009; Solomon et al., 2011; Becker et al., 2013; Dzvinamurungu et al., 2013; Rose 2016; Sibanye Stillwater RR 2020; Corin et al., 2021). The platiniferous unit has highest PGE and pentlandite association with pyrrhotite; where the BMS hosting the PGEs commonly occur within the interstitial silicate host matrix along cracks and cleavage planes and at grain boundaries adjacent chromite phases (Miller et al., 2005; Becker 2009; Smith et al.,

Table 3
Variation of the bulk modal composition (wt %) of gangue/host mineralisation in the Bushveld Igneous Complex ore bodies.

Ore Body	Enstatite (orthopyroxene)	Anorthite (Plagioclase)	Augite (Clinopyroxene)	Chromite	Amphibole	Serpentine	minor phases	References
Merensky (wt %)								
	68	18	8	1	1	0.3	3.7	Rose 2016
	60	20	15	–	–	–	–	Schouwstra et al., 2000
	46	33.4	7.8	5	0.7	1.2	6.3	Solomon et al., 2011
	51	17	4.4	3.3	0.5	0.3	23.7	Brough et al., 2010
	59*	30	–	3.2	3.5	0.03	4.27	Smith et al., 2013
	53–67	16–31	6–8	0.45–1	–	0.33–5^	5–9	Dzvinamurungu et al., 2013
	24.6	4.4	10.3	0.8	6.8	10.6	38.5	Becker et al., 2014
	32–36	9–11	7.7	0.8–4.1	4–5	18–19	17–26	Molifie 2021
UG2 (wt%)								
	18	10	3	65	1	1	2	Rose 2016
	13	14.5	0.9	62	0.2	1.6	7.9	Solomon et al., 2011
	20	7	0.8	70	0.3	0.06	1.83	Little et al., 2017
	15–20*	3–5	–	40–50	–	–	–	Hay and Roy 2010
	16	25	1	49	–	0.27	8.5	Dzvinamurungu et al., 2013
	20*	26	–	49	–	–	3.2	Becker et al., 2008
	23	16	2	52	0.9	0.1	5.89	McFadzean et al., 2015
	5–30*	1–10	–	60–90	–	–	–	Schouwstra and Kinloch, 2000
	24	7	2	61	–	–	–	Becker et al., 2013
	16	17	1.2	60	1.2	0.3	4.4	Little 2016
Platreef (wt%)								
	36	–	13	0.8	–	22.7	15.5	Mwase et al., 2014
	17–71	2–50	4–20	<1–21	<1–3	<1–25	–	McCutcheon 2013

NB: Minor phases may include minerals that are > 1 wt% found in a particular ore body but may be < 1 wt% in the other ore bodies. *value was provided to include both orthopyroxene and clinpyroxene. ^presented as serpentine and talc.

Table 4
Variation of the bulk modal composition (wt %) of the dominant minor phases from Table 3.

Ore Body	Talc	Chlorite	Mica	Quartz	Olivine	Sulfides (BMS)	References
Merensky	0.1	1.5	0.7	0.5	–	1.51	Solomon et al., 2011
	–	–	0.23	0.23	–	0.81	Rose 2016
	0.1	0.1	0.9	–	1.1	0.89	Smith et al., 2013
	0.3	0.6	1.8	0.7	17.3	1.4	Brough et al., 2010
	18	5.1	0.9	0.3	–	0.2	Becker et al., 2014
	5–10	3	1.5	–	–	0.3	Molifie 2021
UG2	0.3	2.8	0.7	0.3	–	<0.41	Solomon et al., 2011
	2	0.4	0.6	–	1.1	0.16	McFadzean et al., 2015
	–	–	0.35	0.07	–	0.04	Rose 2016
	0.4	1.6	0.4	–	1.8	0.2	Little 2016
	0.01	0.34	0.16	–	0.78	0.03	Little et al., 2017
	1–3	–	–	–	–	<0.1	Hay and Roy 2010
Platreef	5.7	3.2	–	–	–	4.4	Mwase et al., 2014
	<1–4	<1–11	<1–4	<1–9	1–3	1–10	McCutcheon 2013

2013; Rose 2016). The PGE minerals in the horizon are largely sulfides, tellurides and partly arsenides, and ferroalloys with historical grades and grain sizes range between 1.6 and 8 g/t and ~ 3.4 – 43 µm where grain size may even reach 150 µm in some regions (Schouwstra et al., 2000; Xiao and Laplante 2004; Waldeck, 2007; Hay and Roy 2010; Rose 2016). The Merensky mineralogy has prominent variations in different facies which may result in erratic PGE grade and grain size in the BIC limbs (Smith et al., 2013). The general process mineralogy characteristics of the Merensky horizon are its slightly coarser PGM grain size, low chromite presence, and higher and coarser BMS tenor (Becker et al., 2013; Dzvinamurungu et al., 2013; Sahu et al., 2021).

In regions where the Merensky Reef lithological stratigraphy is interlayered with the Pseudo Reef bodies (i.e. the Upper Pseudo Reef, the Pseudo Harzburgite Reef, and the Lower Pseudo Reefs), these Merensky associates are termed "Silicate Reef". These horizons are generally weathered/oxidized near-surface deposits (Ramonotsi 2011; Molifie 2021), where the BMS are intergrown in the host silicate structure via attachment. The major PGE compounds are alloys, arsenides, and sulfides followed by lesser amounts of tellurides and electrum - occur as discrete PGM contents showing evidence of re-distribution through solid solution substitution (Bulatovic, 2010). This Merensky interlayered horizon contain lower BMS (0.2 wt%) and PGE (~0.48 – 1.73 g/t 3E, 0.64 – 1.88 g/t 6E) contents compared to the "normal" Merensky horizon (Ramonotsi 2011; Becker et al., 2014; Musonda 2015; Molifie 2021; Sedibelo, 2022).

2.2. *Upper group 2 Reef ore body characteristics*

The Upper Group 2 (UG2) Reef is a pyroxenitic layered unit predominated in the main ore bearing zone by chromitite units (Hay and Roy 2010; Rose 2016; Little 2016; Corin et al., 2021). The dominant gangue mineralisation are chromite, aluminium silicates, minor secondary mineral assemblages, and to a much lesser extent traces of oxides. The lithological unit of chromite, chromitite, consists of about 30 –

50% Cr_2O_3 and may even be as high as 60 – 90% Cr_2O_3 disseminated in variable UG2 facies in the BIC. The primary magnesium alumino-silicates are pyroxenes (enstatite) and plagioclase (anorthite), while the altered hydrous silicate species are mainly amphiboles, chlorite, serpentine, and talc (Table 3; McCall 2016; Little 2016). Alteration features in the UG2 horizon shows hydrous silicate replacement of the primary silicates usually cross cutting veins along cleavage planes. These features may vary in the western and eastern limbs. Where BMS are in close association with the primary alumino-silicates, hydro-thermal alteration engulfs the sulfide minerals - the main PGE host (McCall 2016). The base metal sulfides mineralisation is sparse representing < 0.03 – 0.2 wt% of the UG2 Reef (Nel et al., 2005; Becker et al., 2008; Greet 2009; Hay and Roy 2010; Solomon et al., 2011; Dzvinamurungu et al., 2013; McCall 2016; Sibanye Stillwater RR 2022). The BMS, entrapped in chromitite layers, exhibit preferential association with chromite as discrete BMS aggregate phases relative to the silicate gangue associates in the main mineralized zone, where pentlandite - the most abundant BMS in the horizon - exhibits the highest association with the PGMs (Rose 2016; McCall 2016).

The principal platiniferous mineralisation in the UG2 horizon are PGE-sulfides and to a lesser extent PGE-alloys with the remainder in lesser amounts being arsenides, antimonides, and tellurides (Shamaila and O'Connor, 2008; Hay and Roy 2010; Corin et al., 2021). The platinum minerals here are markedly characterised by small grain size and exhibit a bimodal average size distribution determined by their host: where in the base metal sulfide minerals the grain size is about 10 – 20 μm, those directly attached or engulfed in the silicates are about 2 – 5 μm (Jones 2005; Hay and Roy 2010). The PGM typical grain size is populated below < 10 μm size fraction - where major deportment is < 3 μm - and are largely finely disseminated (Penberthy et al., 2000; Nel et al., 2005; Chetty et al., 2009; Rule and Schouwstra 2012; Rose 2016; McCall 2016). Coarse PGE grains > 20 μm are rare and consist of about 5% of the PGEs in the platiniferous suite (Nel et al., 2004; Little 2016). The typical head grade of the UG2 is 4 – 10 g/t but averages more around 4 – 5 g/t (Schouwstra and Kinloch, 2000; Hay and Roy 2010; McCall 2016; Corin et al., 2021).

2.3. Platreef ore body characteristics

The Platreef PGE bearing horizon - located in the northern limb of the BIC - is a complex polymetallic igneous and metamorphic lithological assemblage with main rock types being pyroxenites, harzburgites, norites, serpentinites, and calcsilicates (Shackleton et al., 2007; McCutcheon, 2013; Klemd et al., 2020). The major PGM host are the silicates, sulfide minerals, and serpentinised alteration assemblages. The predominant host may vary in different regions across the reef resulting in the head grade and distribution of both BMS and PGM to be erratic (Schouwstra and Kinloch, 2000; Kinnaird et al., 2005; Shackleton et al., 2007; Mwase et al., 2012, McCutcheon 2013, Mwase et al., 2014). The PGE content in the reef is low but enriched in sulfide minerals: PGE grade may range between 0.99 g/t 3E – 5 g/t 6E, where the ores are distinguished by discrete metallic PGM phases and the abundance of high palladium deportment (Hutchinson and Schürmann, 2004; Hutchinson and Kinnaird, 2005; Adams et al., 2011; Mwase 2016; Mwase and Petersen 2017; Klemd et al., 2020; Corin et al., 2021; Singh et al., 2022; Sema et al., 2022). The PGE mineralisation generally includes PGE - tellurides, arsenides, alloys, and minor occurrence of sulfides and sulfarsenides (Shamaila and O'Connor, 2008; Adams et al., 2011; McCutcheon 2013; Mwase 2016). The PGM grain size is concentrated in the fine grained fractions < 3 μm; rare coarse grains (up to 35 μm) are possible (Adams et al., 2011; Chetty et al., 2009; McCutcheon 2013).

The base metal sulfide content ranges between ~ 0.21 – ~0.5%, of the host gangue lithology, with sporadically elevated values as high as up to 10% in the Tweefontein lithological units (McCutcheon 2013; Mwase et al., 2014; Klemd et al., 2020; Singh et al., 2022; Sema et al., 2022). Orthopyroxene, plagioclase, and minor clinopyroxene are major mineral species of the unaltered gangue magmatic silicates; while alteration mineralisation exists with the serpentinite being the dominant alteration species and traces of other associated mineral species including iron-oxides, carbonates, quartz, micas, chromite, and garnet (Shackleton et al., 2007; McCutcheon, 2013; Mwase et al., 2014).

3. Metallurgical treatment of platinum group minerals

Metallurgical plant design and processing of BIC PGE ores is primarily dependent on the ore's physical, petrographic, and mineral characteristics (Becker et al., 2008). The processing of PGE-bearing ores is challenged by its complex mineralogy and the inherent complex operation that requires several unit stages including pre-treatment steps. The typical PGE recovery from minerals to pure metals in South African concentrators involves (a) size reduction: crushing and milling of run-of-mine (ROM) ores to liberate minerals of interest (b) mineral separation: froth flotation to obtain PGM concentrate (c) high-temperature smelting and conversion, followed by (d) hydrometallurgical refining processes to produce saleable metals (Jones 2005; Crundwell et al., 2011; Little 2016).

Ore received from the ROM is usually crushed to ~ 90 mm and is fed to the comminution circuits to achieve a final grind of 60 – 80% passing 75 μm. Rougher concentrate streams are thickened to 35 – 45% solid by mass and further treated in scavenger, cleaner, and recleaner banks, while tailings from the final rougher streams are deposited in tailing pounds (Buys et al., 2004; Hay 2010; Rose 2016). Gravity, dense medium, and/or magnetic separation techniques may also be used along with flotation in PGE concentration circuits (Bryson, 2004; Xiao and Laplante, 2004; Panda et al, 2018; Sahu et al., 2021). However, these separation techniques are not typical in the BIC PGE primary concentration circuits but may be host mineralisation specific (Letseli et al., 2018).

The final concentrate from the flotation circuits is dried, followed by high temperature (1500 °C) smelting to obtain two separate melt phases: silicate melt (slag) and sulfide melt (matte) which are tapped separately. The smelted matte undergoes iron and sulfur removal in the converting stage, and the converter matte containing the BMS and PGE go through pressure oxidation (POX) to recover the BMS (Ni, Cu, Co) in solution for base metal refining. The POX residue high in PGE content is refined through different hydrometallurgical separation and purification processes to obtain saleable PGEs as pure metals (Cramer, 2008; McCall 2016; Little 2016; Sinisalo and Lundström 2018; Sahu et al., 2021). The hydrometallurgical separation processes involve precipitation, dissolution, distillation, solvent extraction (SX), and ion exchange (IX) at different stages of the precious metal refining flowsheet (Tatarnikov et al 2004; Belova, et al., 2007; Crundwell et al., 2011; Snyders et al., 2013; Schoeman et al., 2012, 2017; Sinisalo and Lundström 2018).

The BIC PGE concentrators are usually configured to suit the mineralogy available in the specific ore body of interest and it is not straight forward but conforms to the generic flowsheet in Fig. 4. The figure also shows the estimated grade of the PGM value chain as well as platinum losses at each unit stage. The major losses of Pt occur largely in mining (i.e. open pit or underground), accounting for about 27 – 28% before processing and the mineral concentration stages where 13 – 20% value loss occur to the tailings during flotation concentration (Ndlovu 2015). Value loss along the smelter and conversion stages is about ~ 1%. Noteworthy, the smelter is usually fed with a blend of concentrates from several different concentrators, indicative of a more generic process. On the other hand, concentration circuits are configured to the specific ore body being mined and are further optimised by readjustments due to the variability of the valuable mineral in the ore body as mining progresses.

The mineralogy of the major BIC reefs varies significantly, as evident by the modal abundance of the major gangue composition in Table 3. Therefore, the selection of a primary metallurgical process route for optimal recovery is correlated to the mineral and textural characteristics

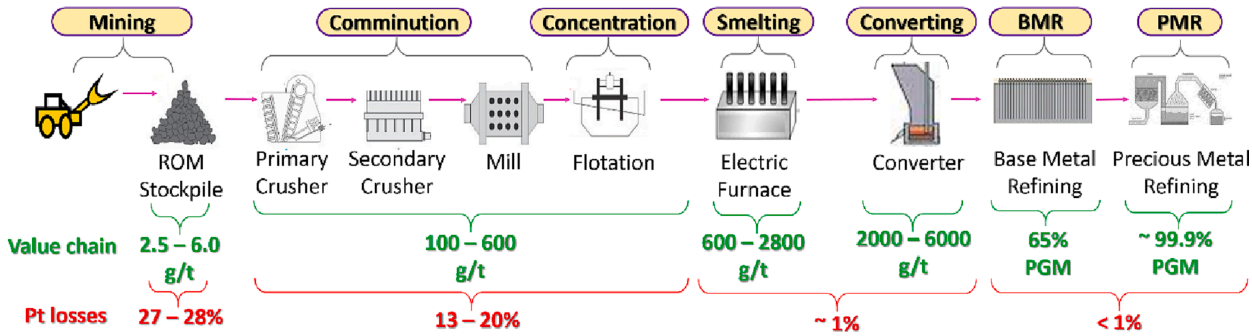

Fig. 4. A generic platinum group element flowsheet option indicating value chain (green annotation) and platinum losses (red annotation) at each unit stage (Vermaak, 1995; Cole and Ferron, 2002; Merkle and McKenzie, 2002; Jones 2005; Crundwell et al., 2011; Ndlovu, 2015; Mwase, 2016; McCall, 2016; Sinisalo and Lundström, 2018).

of PGM and BMS, geological positioning, host lithology gangue mineralisation, and the potential mining cut dilution (Becker et al., 2008; McCall 2016). Considering that gangue minerals constitute about 96 – 99% of the ore metallurgical feed, the inherent primary treatment flowsheet is driven by the mineral characteristics of the dominated gangue, the potential PGM recovery, energy and reagent input requirements, and asset reliability (Ndlovu 2015; Little 2016).

The Merensky Reef is known to be less problematic to process compared to the UG2 and Platreef ore bodies (Hay 2010). Notwithstanding, the UG2 and Platreef – possessing complex mineralogy and more difficult to process – are currently the primary sources of PGE in South Africa (Rule and Schouwstra 2012; Mwase et al., 2012; Corin et al., 2021).

3.1. Concentration circuit

Froth flotation concentration is a mineral separation technique that takes advantage of the surface properties of minerals. It is the primary concentration separation technique considering PGEs are finely disseminated in association with BMS present in the ore; and, equally, the PGE characteristic fine to ultrafine grain size in the BIC ore bodies (Rose 2016; Sahu, et al., 2021). The PGMs associated sulfide mineralogy are easily floated; conversely, PGMs locked in silicates, at boundaries of chromite (Cr_2O_3), or liberated ultrafine grains take longer to float - as a result of the lower statistic likeliness for a less hydrophobic mineral grain to attach (and stay attached) to a bubble, which is not a chemical kinetic phenomenon - and may eventually become rejected to the tailings (Penberthy, et al., 2000, Shamaila and O'Connor, 2008, Becker et al., 2014). More so, alteration PGE silicate hosts, phyllosilicates, in weathered BIC ores are known to be problematic during froth flotation (Becker et al., 2012, 2014; Letseli et al., 2018; Molifie 2021). Flotation recovery of weathered PGM ores is erratic with recovery between 25 and 92% (Letseli et al., 2018). According to Ramonotsi (2011), average metallurgical recovery of these type of near-surface altered ores is 35%. It has been proposed that the erratic recovery is a function of mining depth of less than 40 m (Ramonotsi 2011; Letseli et al., 2018). The primary treatment of such ore types results in a significant proportion of valuable mineral being rejected to the tailings. Ramonotsi (2011) reports that the targeted plant tailing grade in the altered Merensky (Silicate Reef) flotation tailing was 0.5 g/t, but the reported tailing grade were an average grade of 1.3 g/t from an average head grade of 1.89 g/t.

In general, typical flotation performance of the BIC ore bodies is in the range of 70 – 88% recovery for 4 – 5 g/t 6E PGE head grade where high recoveries are only achieved routinely in highly optimised circuits (Bryson, 2004; Hay 2005; Rule et al., 2008; Bulatovic, 2010; Hay 2010; Rule and Schouwstra 2012; Rose 2016), while erratic flotation recovery from alteration ores may be in the range of around 35 – 65% (Ramonotsi 2011; Letseli et al., 2018). Concentrate grade for Merensky is about 80 – 200 g/t and 140 – 450 g/t for UG2 (Hay 2010; Rose 2016), while concentrate grades from the lower grade Platreef ranges about 56 – 120 g/t PGE (Cramer, 2008; Mwase et al., 2012). However, in other investigations Adams et al. (2011) and Liddell and Adams (2012) reported Platreef concentrate grades as low as ~ 5 g/t PGE. The efficacy of flotation separation is dependent on the effective liberation of the valuable minerals for reagent attachment. Over the last two decades, major PGE producers embarked on optimisation campaigns to improve recovery whilst reducing % Cr_2O_3 to < 2.5% in the final flotation concentrate for the UG2 ore feed (Nel et al 2004; Vos et al., 2007; Hay 2010; Rule and Schouwstra 2012). The decline in milled head grades drove advancement in the primary treatment. Other factors also include the complex mineralogy emanating from UG2 and Platreef ore types and inconsistent PGM recoveries – due to the inherent complex mineralogy of ore fed to concentrators (Corin et al., 2021). The UG2 reef contains about 40 – 70% chromite which renders processing complexities in the concentration circuits. More so when operated in a closed liberation circuit resulting in over grinding of the fine dense chromite particles (Nel et al 2004; Little 2016).

The PGM industry in South Africa achieves optimal liberation by applying the two-stage mill float–mill float (MF2) circuit ideal to treat UG2 ores (Fig. 5; Hay and Schroeder 2005; Rule and Schouwstra 2012; Little 2016). Prior to the MF2 circuit, the mill-float, MF1, circuit (Fig. 5) was the primary concentration route for the Merensky mill feed (Hay 2005). However, the friable mineral characteristics of the chromitite makes the MF2 circuit more effective avoiding recirculation and producing fines in closed circuit MF1 operations (Nel et al., 2004). The MF2 circuit typically uses ball mills for both primary and secondary grinding. The primary grind is usually coarser to liberate the PGMs, essentially from their annealed chromitite host, and the ground ore is then floated, followed by treatment of the primary rougher tails in the secondary grind, which targets smaller PGE grain sizes locked within the coarser silicates, followed by their recovery in the secondary flotation rougher circuit (Hay and Roy 2010; Rule and Schouwstra 2012; Little 2016). The successes of the MF2 configuration is influenced by (a) the dominant friable chromite that requires only minimal grinding effort to achieve liberation of the PGM along the chromite grain boundaries. (b) Effective classification prior to the secondary grinding would result in liberation of only coarse silicate gangue containing intergrown PGM in the silicate crystal lattice (Nel et al., 2004; Little 2016).

The established standard grinding size for optimal metallurgical recovery in the South African PGM industry is reported to be 55 – 65% passing 75 µm for Merensky circuits (i.e. MF1; Hay and Roy 2010). Grind size for MF2 circuits of all other complex mineral reefs is 30 – 40% passing 75 µm for primary grind and 60 – 80 wt% passing 75 µm for the final/secondary grind (Cramer 2001; Nel et al., 2004; Hay 2005; Hay and Roy 2010; Little 2016; Rose 2016). Meanwhile, value mineral liberation via finer grind in the MF2 open circuit configuration is energy intensive, incurring higher power cost (Nel et al., 2004, 2005; Hay 2010; Corin et al., 2021).

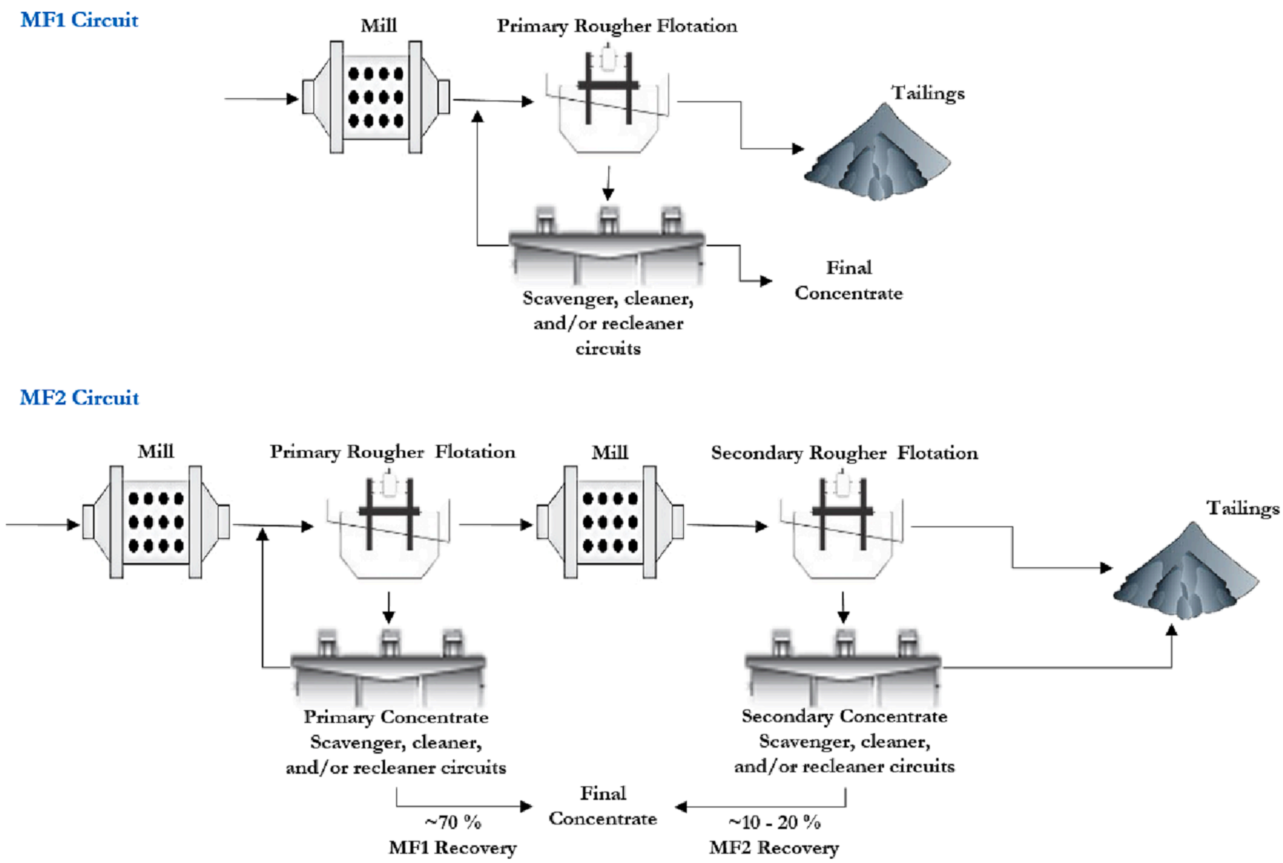

Fig. 5. Mill-float (MF1) and mill-float-mill-float (MF2) concentration circuits adapted after (Hay, 2005).

The metallurgical performance of the UG2 and Platreef milled feed is dependent on the extent of silicate association with the PGMs, where poor flotation recoveries are a function of high PGM association with silicates; hence incomplete liberation, even in the optimised MF2 circuits, results in value rejection to the tailings with grades up to about 1 g/t (Nel et al., 2004; Bryson, 2008; Rule 2010; Bushell 2012; Becker et al., 2014; Little 2016). However, the introduction of stirred mills in the PGM industry essentially addressed the issue of liberation efficiency. The two main applications of stirred mills along concentrators' circuits are ultrafine grinding (UFG, 80% passing < 20 μm) in concentrate cleaning/recleaning stages and mainstream inert grinding (MIG, 80% passing < 45 μm); where the MIG (in by-pass milling circuit) improved the liberation of partially liberated PGM locked within silicate crystals (Rule 2010; Rule and Schouwstra 2012). According to Rule and Schouwstra (2012) the introduction of the MIG stirred mill significantly reduced value rejection to the tailings to about 0.5 – 0.6 g/t 4E PGE at a plant recovery of 88%.

Noteworthy, plant recovery efficiency as it relates to reporting "high % extraction" - i.e. 85 – 88% - is always relative to the plant feed grade, which varies widely. This becomes important when focussing on what is left behind in tailings. For instance, the extractable fraction of a plant feed grade of 3 g/t is different relative to another plant feed grade of 5 g/t; hence, it becomes misleading to holistically consider overall plants recovery efficiency of 88% as "high % recovery" when this still leaves behind a tailings grade of 0.5–0.6 g/t, whereas the same tailings grade would correspond to only 80 – 83% recovery of a plant feed grade of 3 g/t. Given the current available technologies, literature studies, and companies' reports, it must be suspected that a tailings grade of 0.3 – 0.5 g/t 4E PGE is in general not extractable by flotation from any ore or tailing re-treatment process, irrespective of the feed grade. This is an important gap in the reporting of the PGE 'resource' in tailings materials.

4. Value rejection to tailings

4.1. Platinum group minerals deportment and economic potential in tailings

The recovery of PGM from its polymetallic low-grade mineralogy is complex, even more so for tailing materials containing<0.01% mass percent of value minerals in multiple associations. Tailings emanating from flotation circuits of different PGM bearing reef types (Merensky, Platreef, or UG2 Reef) and plant units (smelter slags) are deposited in tailing dams over the life-of-mines or until the impoundment total capacity is reached. Historical dormant tailings predominately contain processed materials from the Merensky Reef, while recent tailing deposits contain more of Platreef and UG2 Reefs along with the Merensky processed streams (Vogeli et al., 2011). Tailing streams inevitably possess a heterogeneous mineral distribution. The low-grade tailings vary in value content, which depends on the operational efficiency of concentrator circuits and feed material mineralogy (Turan et al., 2020). The knowledge of what influences valuable minerals deportment to the flotation tailings - even in optimized plant operations - require an understanding of the rejected value mineral characteristics, which is considered in this section.

4.1.1. Mineralogical and chemical characteristics of tailings

The major mineralogy of concentrators' feed and tailing of a typical flotation circuit are relatively similar (Becker et al., 2013; Rose 2016); however, because processing plants obviously concentrate ore from different lithologies and mining sections, the bulk tailing materials deposited in dams or impoundments may have significant mineralogical variations. Based on typical X-Ray Fluorescence (XRF) chemical and elemental composition of the BIC tailings from PGM plant final tailings as well as chromite recovery plant (arising from PGM tailings), the BIC tailings contain significant amounts of aluminium, magnesium, chromium, and iron as well as moderate concentrations of titanium (Table 5). Silicate and oxide minerals dominate the mineralogy of South African BIC tailings: containing substantial quantities of orthopyroxene (enstatite), plagioclase (anorthite), and chromite (including spinel minerals). The UG2 tailing streams are dominated in chromite spinel and silicates; while the Platreef and Merensky tailing streams are predominantly silicate gangues – pyroxenes and plagioclases. The tailing mineralogy resonates with Table 3 (in section 2) showing variation in the composition of the major mineral phases along different sub-facies of the major BIC PGM ore bearing bodies. Other locally important minerals occurring in lesser amounts in these tailings are clinopyroxene (augite), amphibole (hornblende), olivine, mica and secondary altered silicates (serpentine, talc, chlorite) – in minor to trace amounts (Dawson 2010; Rabatho et al., 2010; Vogeli et al., 2011; Meyer et al., 2014; Mohamed et al., 2016; Rose 2016; Amponsah-Dacosta 2017; Setlhabi et al., 2019). The secondary alteration silicate minerals readily occur in significant amounts in the flotation tailings of near-surface or shadow weathered PGE deposits (Ramonotsi 2011; Letseli et al., 2018; Molifie 2021).

Particle size distribution of the BIC tailings vary depending on the primary treatment at plant operations (Vogeli 2012; Amponsah-Dacosta and Reid, 2014), i.e. comminution-recovery techniques, the reef location, the reef inherent mineralogy (as well as sub-facies variation), and the re-treatment type (i.e. tertiary treatment) prior to the final tailings deposition (Mohamed et al., 2016). The particle size distribution in Table 6 shows that the final tailing materials generated from Merensky circuits are relatively coarse-grained, while those originating from individual processing of the Platreef and UG2 Reefs are fine-grained. However, tailing material from composite UG2 and Merensky Reefs possess coarser size fractions compared to particle distribution from the individual reefs tailing material. The heterogeneity of mixed reef tailings adds to the complexity of PGM tailing mineralogy, in particular due to the common industrial practice of not depositing tailings in separate TSFs, even if the parent ore materials are processed in separate circuits (Vogeli et al., 2011; Hay 2005; Rule et al., 2008; Amponsah-Dacosta 2017). On the other hand, one advantage of valorising tailings is the fact that the materials are already milled to 80 – 85% passing < 150 μm, thereby avoiding extensive milling that is a key cost factor in the primary concentration process.

4.1.2. Valuable minerals association, liberation, and deportment in tailings

Comminution and liberation stages release valuable minerals from the interstitial or grain boundary of their gangue hosts (Corin et al., 2021). The coarser the value mineral grain, the easier are liberation and subsequent flotation separation. Conversely, the finer the value mineral grain the more difficult it becomes to recover the value from the gangue matrix. This is evident in the processing of the Merensky Reef that comes with ease due to their large PGM grain, low chromite content, and common occurrence with floatable BMS (Becker et al., 2013; Rose 2016). In plant operations, good sulfide recovery is suggestive of high liberation efficiency as well as improved PGM recovery (Wiese et al., 2006; Dzvinamurungu et al., 2013). Sulfide mineral liberation is often used to infer PGM liberation - largely for hidden or latent PGEs attached to or locked within the sulfide lattice (Godel et al., 2007; Zhu et al., 2010; Rose 2016; Sinisalo and Lundström 2018). However, this correlation holds true only for value recovery in the primary mill-float (MF1) concentrate. Using BMS flotation to absolutely infer PGE flotation recovery may be erroneous, considering that PGMs also occur as discrete mineral phase and may not necessarily be associated with the sulfides after extensive liberation from the host gangue or sulfides in the secondary grinding or inert MIG regrind circuit (Rule 2010; McCall 2016). Hence, liberated PGM losses in the fine grain < 5 μm fraction usually show no correlation to the sulfides liberation (Rule, 2011; Little 2016; Singh, 2016).

Value PGE minerals are predominantly associated with silicates in the tailings and occasionally at the interstitial boundaries around chromite phases (Dawson 2010). PGM directly associated with the silicates, i.e. non-floatable primary silicates (pyroxenes and plagioclase), float very slowly and ultimately deport to the tailing in partial liberated grains or enclosed within the gangue minerals (silicates/oxides) in significant proportions (Chetty et al., 2009; Rule 2010; Smith et al., 2013). The PGM-silicate association renders the gangue mineral group in the processed tailings PGM grade possibly recoverable via fine inert regrinding (Rule and Anyimadu 2007). However, a major challenge arises when the PGMs deport to the ultrafine fractions – associated with the silicates instead of their better floating sulfide associates (Rule 2010; Singh, 2016). In an investigation using magnetic separation to recover value from mixed UG2 and Merensky tailings, Rabatho et al. (2010) found that value PGEs (Pt and Pd) were contained in chromite spinel mineral phases, but the authors did not provide results of the silicate rejects. Rule and Anyimadu (2007) found that 0.35 g/t 4E of a 0.5 g/t 4E plant tailing grade were locked-in PGM particles while the other 0.15 g/t 4E was liberated PGM and PGM/BMS associates. Nel et al. (2005) presents four possible categories in which PGM grains are likely to occur: liberated, PGM/BMS association, PGM occurring at grain boundaries of host gangue phases, and PGM fully enclosed in the silicates. The latter two categories are most difficult to float and likely to be found in tailings – accounting for up to 55% of PGM reported in the material (Nel et al., 2004). One major characteristic of the BIC PGM is their fine dissemination largely reporting in the < 10 μm fraction (Nel et al., 2005; Rule and Anyimadu 2007; Smith 2010; Corin et al., 2021; Singh et al., 2022; Sema, et al., 2022). Tailings of highly weathered ores processed from near-surface deposits contain substantial quantities (amounting to 64% of the total PGM) in the tailing being unliberated, while the liberated (22%) ones in association with the BMS possess grain size deporting to < 2 μm and those at grain boundaries (9%) are in minor occurrences (Ramonotsi, 2011). Typical PGM average grain size of UG2 plant final tailings is reported in the P50% range at 5.5 – 5.7 μm possessing liberation degree ranging 20 – 35% (Rule 2010, 2011; Rule and Schouwstra 2012). Rule and Anyimadu (2007) indicate that PGM in the ultrafine

Table 5
Bulk XRF chemistry of South African platinum group mineral tailings.

Tailing Source	Operation	SiO_2	MgO	Al_2O_3	Fe_2O_3	Cr_2O_3	CaO	Na_2O	TiO_2	NiO	References
Merensky	Northam	47.8	21.9	7.87	13.1	2.25	4.97	0.75	0.29	0.13	Vogeli et al., 2011
	BRPM	49.9	14.6	14.4	8.85	0.87	8.73	1.2	0.24	0.08	Vogeli et al., 2011
	Rustenburg (Waterval)	46.31	13.52	14.17	10.39	5.05	7.41	1.14	0.33	0.22	Amponsah-Dacosta 2017
Platreef	Mogalakwena	50.03	19.46	8.84	10.52	0.43	7.55	1.39	0.20	0.13	Amponsah-Dacosta 2017
UG2	–	16.49	9.90	6.85	31.85	26.24	6.58	0.17	0.61	0.25	Letseli et al., 2018
	–	36.63	15.8	14.66	13.26	12.27	4.83	1.03	0.44	–	Setlhabi et al., 2019
UG2 & Merensky	Two Rivers	17.4	13.6	12.2	23.3	31.9	2.5	0.3	0.7	–	Mohamed et al., 2016
	Amandelbult	29.77	15.57	12.64	20.14	16.40	3.54	0.66	0.54	0.14	Amponsah-Dacosta 2017
	Impala	39.40	14.68	13.62	14.66	9.57	5.90	0.90	0.43	0.10	Amponsah-Dacosta 2017
	Union Section	30.16	16.13	10.58	19.47	18.97	2.82	0.51	0.53	0.12	Amponsah-Dacosta 2017
MMZ*	Nkomati	42.74	21.20	6.51	11.47	2.58	7.53	0.76	0.42	0.10	Amponsah-Dacosta 2017

* Main Mineralized Zone.

Table 6
Particle size distribution (μm) information of plant final tailings or tertiary scavenger flotation feed.

Tailing Source	BIC/Other Location	Operation	90%	80–85%	70%	50–60%	10%	References
Merensky	Western limb	Lonmin*	283	–	–	84	–	Meyer et al., 2014
	“	Platinum Mile (UFG)		80	–	37	–	Rule et al., 2008
	“	Rustenbuurg (Waterval)	215.18	–	–	51.38	7.66	Amponsah-Dacosta 2017
	“	Northam	237.5	–	–	72.1	7.3	Vogeli 2012
	“	BRPM	137.5	–	–	25.1	2.3	Vogeli 2012
	“	Impala	363.6	–	–	126.3	18	Vogeli 2012
	“	Lonmin*	293	–	–	87.4	7.4	Vogeli 2012
Mixed UG2 & Merensky	Eastern limb	Two Rivers	328.7	–	–	131.4	26.4	Mohamed et al., 2016
	Western Limb	Impala (dam 4)	582.14	–	–	221.08	17.7	Amponsah-Dacosta 2017
	“	Amandelbult	431.73	–	–	184.63	62.36	Amponsah-Dacosta 2017
	“	Union	233.52	–	–	42.78	6.84	Amponsah-Dacosta 2017
	–	–	–	–	–	45	–	Rabatho et al., 2010
Platreef	Northern Limb	Mogalakwena	197.39	–	–	61.03	5.41	Amponsah-Dacosta 2017
	“	“	–	–	–	<25		Sema et al., 2022
UG2	Northern Limb	Chromite Recovery Plant	–	75	–	–	–	Letseli et al., 2018
	Western limb	–	106	75	–	53	–	Setlhabi et al., 2019
	“	Lonmin*	–	110	–	–	–	Little et al., 2017
	“	Lonmin* (tertiary UFG)	–	70	–	–	–	Little et al., 2017
	“	PGM Tailing Re-treatment	–	–	106	75	–	Ross et al., 2019
	“	Pilot plant (UFG) operation	53	–	–	17	–	Becker et al., 2013
	“	Amandelbult	–	–	–	51	–	Rule and Schouwstra 2012
	“	Lonmin*	–	106	–	53	–	Little 2016
	Eastern Limb	Two Rivers	–	75	–	–	–	Rose 2016
MMZ	MMZ	Nkomati	312.03	–	–	99.8	17.33	Amponsah-Dacosta 2017

* Lonmin is now owned by Sibanye Stillwater.

particle fraction are liberated and those in the true flotation size fraction (+53 μm) are partially liberated; they further argue that the major challenge facing industrial flotation circuits is floating the PGEs that are in the ultrafine < 5 μm fraction. This argument is backed by subsequent literatures (Rule, 2011; Singh, 2016). Essentially, the PGM particle size known to represent the flotation process (i.e. true flotation) ranges from −75 μm to + 38 μm (Adams et al., 2011; Dzvinamurungu et al., 2013). It is reported that valuable minerals locked in or attached to gangue particle size in the fines (<38 μm) and coarse fractions (>106 μm) are difficult to be recovered during flotation (Nel et al., 2005; Rule 2010; Muganda et al., 2012; Little 2016). Rule and Schouwstra (2012) report that about 20 wt% of the tailing materials possessing PGM grains deports to the fine to ultrafine particle fraction, while about 50 wt% deports to the coarser (+106 μm) fraction and about 30 wt% in a broader flotation particle range. Elsewhere, particle size distribution from the secondary rougher tailings of a UG2 concentrator reports 35 wt% in the fine to ultrafine fraction (<25 to < 10 μm), 50 wt% in a broader flotation particle size range (-106/+25 μm), and 15 wt% deporting to the coarser size (+106 μm) region (Little 2016). Little (2016) also found that PGM deportment in each fraction was 44% in the fines to ultrafine, 41% in the −106/+25 μm flotation range, and 15% in the coarser size. The author further reports that 22% of the initial 4E PGM milled feed (4.42 g/t) deported to the concentrator final tailing. Thus, Rule and Schouwstra (2012) and Little (2016) plant reports confirm that PGE minerals in the true flotation particle size (-75 μm to + 38 μm) also become rejected to the tailings – as was mentioned in earlier works by Duarte et al. (2004).

The PGE mineral speciation in industrial processed tailings may occur in the order of PGE-alloys, PGE-sulfides and lesser amounts of PGE arsenides and PGE-tellurides (Smith 2010, Molifie 2021). Generally, PGE-alloys are known to be slow floaters, which makes it plausible for their rejection to tailing, more so than readily floatable PGE-sulfides (McCall 2016). Modal PGM association with BMS in Merensky Reef processed tailings was reported to have about ~ 49% pyrrhotite-PGM association and trace occurrence of the PGMs with the other sulfides.

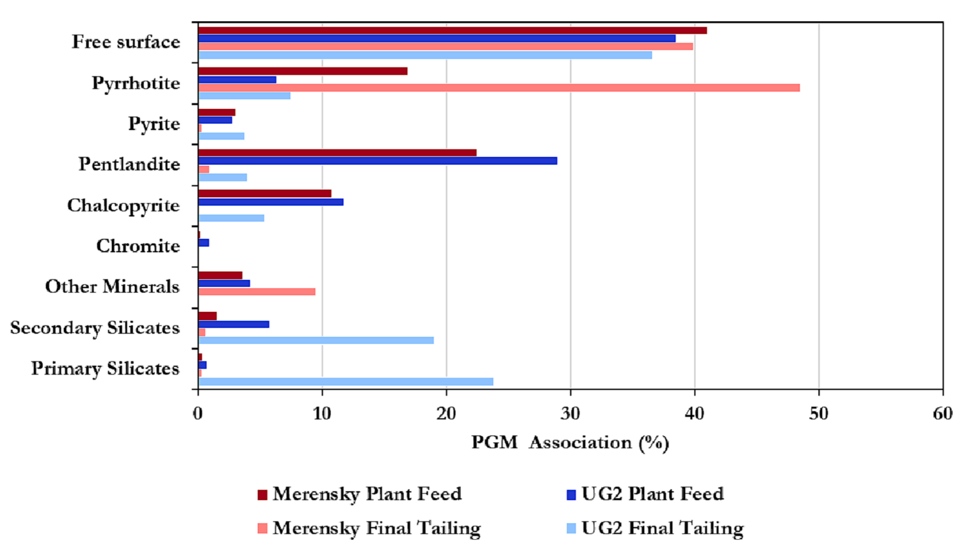

Fig. 6. Plant data illustrating platinum group elements and gold (PGE + Au) association in the feed and tailing streams at the Two River Merensky and Upper Group 2 concentrators. Data obtained from Rose (2016).

For a UG2 plant final tailing the PGM/BMS association was in the order of pyrrhotite (~7%), chalcopyrite (~5%), and similar proportion (~4%) of pyrite and pentlandite (Rose 2016). The PGM + Au association with other minerals in both the plant feed and tailing at Two River mine are depicted in Fig. 6. Importantly, only some of the gold present in a PGE bearing ore entirely occur in association with the sulfides as in the case with the PGMs. It is reported that metallic/free gold and gold captured in the silicate minerals may not readily report to the flotation concentrate but to the tailings – locked in the silicates (Dzvinamurungu et al., 2013). Rose (2016) mineralogical Merensky and UG2 plant investigation further showed that the BMS population in Merensky plant final tailing were readily fine grained (i.e. 80% <46 μm) containing about 56% of the BMS being liberated but rejected to the tailings: of these, pentlandite and pyrrhotite were found to possess liberation degree of 92% and 47% respectively. The UG2 plant final tailings in the same investigation showed a similar BMS population reporting below 21 μm containing about 18% fully liberated BMS in the final tailing stream. In the UG2 tailing stream, pyrite was the most liberated (42%) relative to pyrrhotite and pentlandite (4 – 5%).

Noteworthy, pyrrhotite is an iron sulfide gangue mineral that is not a valuable sulfide mineral – it is usually rejected in flotation circuits of sulfide ores. However, its common association with the valuable sulfides (chalcopyrite and pentlandite – in solid solution) and PGM in the BIC PGM-bearing ores offer the mineral its significance to be recovered along with the valuable minerals in flotation circuits (Miller et al., 2005; Becker 2009; Sema et al., 2022). Nonetheless, pyrrhotite-PGM association is known to be difficult to recover during flotation and may be rejected to the tailings due to their slow floatability (Mishra et al., 2013; Sinisalo and Lundström 2018; Sema et al., 2022). The pyrrhotite deportment in the BIC PGM tailings would therefore suggest the presence of PGEs; more so, within Merensky and UG2 plants final tailings that contain high pyrrhotite concentrations associated with the PGMs (Rose 2016). Pentlandite is another sulfide mineral that may suffer losses to flotation tailings (Wiese et al., 2005). Nickel abundance in tailings occur primarily as pentlandite and at the same time in other forms, tending toward altered pentlandite mineral species such as violarite ($FeNi_2S_4$) or millerite (NiS) (Lamya 2007; Ramonotsi 2011; Rose 2016). Considering the pentlandite solid substitution with pyrrhotite and in other gangue species, nickel locked in silicates/oxides is rarely recovered via flotation (Mathez and Mey, 2005). Pentlandite loss to the conventional treatment final tailings is prevalent in highly weathered/oxidized near-surface PGE-bearing ores (Legrand et al., 2005; Musonda 2015).

4.1.3. *Factors influencing valuable minerals rejection to tailings: Industrial challenges and mitigation*

Valuable mineral propagation to tailings may be dependent on the mineralogy of the material, which would affect the inherent metallurgical performance of the payable minerals present. Here, we outlined several factors that are most likely responsible for valuable mineral rejection to flotation tailings. These include incomplete/partial value mineral liberation, plant stability, slow floating minerals, and surface passivation.

4.1.3.1. Incomplete/partial value mineral liberation. Value PGM and BMS minerals in the tailings are usually found in the middling and fines fractions (Rule et al., 2008). High proportion of the PGMs are associated with the silicates/oxides either as attachment or as fully enclosed grains (Bushell 2012; Rule and Schouwstra 2012; Becker et al., 2014). Prominent in the UG2 circuits is the challenge of partial liberation where the bulk of the PGMs are associated with silicates in the middling and locked categories of both concentrate and tailings (Rule 2010). Moreover, gangue suppression during flotation concentration is also said to serve as the primary means of redirecting valuable minerals (attached/locked) to the tailings (McCall 2016). Value mineral losses occur irrespective of the particle size, where locked-in or partially liberated value particle even in the typical flotation particle size range (-75/+38 μm) or broader flotation size (-106/+25 μm) report to the tailings (Rule and Anyimadu 2007; Corin et al., 2021).

4.1.3.2. Plant operational stability. Flotation inefficiencies and plant instability can cause value losses – i.e. stoppages and start-ups of mills and flotation circuits (Talbot 2004; Rule and Anyimadu 2007; Rule et al., 2008; Eastplats 2022). More so, operational fluctuations in plant performance can also be attributed to ore variability, which affects the concentrator throughput, chemical response (reagent additions and adjustments) and plant control: inherently shifting the plant grade and recovery (Talbot 2004; Rule 2010; Little 2016).

4.1.3.3. Slow floating minerals. Slow floatability as defined in section 3.1 is considered as the lower probability of a less hydrophobic mineral grain to attach and stay attached to a bubble in the slurry where this interaction is not a chemical kinetic phenomenon. Slow floating valuable minerals (i.e. PGE-alloys, PGE arsenides, and pyrrhotite) are known to spend longer time in flotation circuits and subsequently are more likely to report to the tailings (Hay and Roy 2010; Smith 2010; Mishra et al., 2013; McCall 2016; Molifie 2021). Moreover, liberated ultrafine PGMs suffer slow floatability – as a result of insufficient kinetic energy to enable attachment to the bubble surface – and report to the tailings in significant proportions (Penberthy et al., 2000; Rule 2010; Little 2016; Singh, 2016). According to Smith (2010), PGE mineralisation in industrial processed tailings occur as PGE-alloys (44%), PGE-sulfides (32%) and lesser amounts of PGE arsenides (13%) and PGE-tellurides (10%). Cognizant that some value minerals are largely natural slow floaters, valuable mineral floatability is also affected to some extent by partial/incomplete liberation (McCall 2016) and surface coatings – most often affecting fines/ultrafine (Pease et al., 2006). Nevertheless, maximizing flotation recovery from fine/ultrafine fraction using conventional flotation has been a recognized challenge for a long time (Yoon et al., 1989; Miettinen et al., 2010), even more so for ore materials from UG2 and altered near-surface deposits (Rule and Anyimadu 2007; Rule and Schouwstra 2012).

4.1.3.4. Surface passivation. Mineral surface oxidation impairs metallurgical performance; it affects finer particle fractions the most, rendering valuable mineral losses (Pease et al., 2006; Newell et al., 2006, 2007). Surface passivation influencing value mineral rejection to the tailings may derive from any of the four possible categories: 1. lithological oxidation – near-surface weathered ore deposits (Hay and Roy 2010; Molifie 2021), 2. galvanic oxidation – particle-grinding media interaction in conventional steel milling environment where rimming by sulfide minerals occurs due to iron oxide/hydroxide, impeding the hydrophobicity of the sulfide mineral (Miller et al., 2005), 3. atmospheric oxidation – oxygen uptake passivating the sulfide mineral, pyrrhotite, surface at the normal flotation condition. Another factor relating to atmospheric-sulfide interaction stems from the exposure of tailing materials deposited in storage facilities over protracted periods (Newell et al., 2007; Becker 2009; Ross et al., 2019), – i.e. in the event of re-treating legacy/historic tailings – and 4. passivation attributed to gangue slime coating (Ross et al., 2019; Molifie 2021).

4.1.3.4.1. Lithological oxidation. Altered near-surface PGM ores regularly exhibit a lower degree of liberation and hence low flotation recovery (Shackleton et al., 2007). Alteration as a result of near-surface weathering deteriorates the valuable mineral surface chemistry, resulting in partial loss of the mineral-group natural hydrophobicity (Lamya 2007). Poor metallurgical performance in these ore types is attributed to PGM grain remobilisation by the altered mineral species to other forms of slow floating sulfides (millerite, violarite, pyrrhotite), secondary floatable silicates, and oxides. (Hay and Roy 2010). The remobilisation dissociates the valuable minerals from their primary associated minerals

(BMS, silicates, chromite) distinct grain boundaries and preferential fractures. In mineralisation where the sulfides are in close association with the primary silicates, it is reported that alteration to secondary silicates results in engulfing the BMS (McCall 2016). The enveloping effect of weathering creates a layering that hinders the collector's ability to recover the value minerals during flotation (Letseli et al., 2018).

4.1.3.4.2. Galvanic oxidation. Conventional grinding steel media can facilitate a redox environment in upstream comminution (ball milling circuits) where the steel balls can act as anodes in galvanic contact with sulfide minerals and thereby release iron ions into solution, altering the pulp chemistry, and eventually precipitating onto valuable mineral surfaces. The iron oxide/hydroxide passivates the sulfide surfaces, hindering downstream flotation recovery (Buys et al., 2004; Miller et al., 2005; Greet 2009; Rule 2010, 2011).

4.1.3.4.3. Atmospheric oxidation. In addition to steel grinding media coating valuable mineral surfaces through galvanic effects, atmospheric oxidation can also directly passivate the surface of pyrrhotite. Oxidation has far-reaching detrimental effect on pyrrhotite floatability and valuable mineral flotation performance in general (Becker 2009). Given the PGMs are associated with pyrrhotite, and the thermodynamic tendency of sulfide minerals to readily oxidize to ferric oxide/hydroxide or intermediate compounds, the pyrrhotite floats slowly and eventually reports to the tailings as the result of a surface coated with oxidation products (Miller et al., 2005). The iron passivated layering on the pyrrhotite surface is known to proceed at normal flotation conditions, i.e. when exposed to air at pH 9 and room temperature (25 °C). Pyrrhotite hydrophobicity is reported to be readily achieved at pH 3 but increasingly loses its hydrophobic properties and lower contact angle above pH 4.5 up to pH 9.5, rendering the mineral surface hydrophilic with resulting low recovery (Miller et al., 2005). In a comprehensive study of pyrrhotite, Becker (2009) reported that pyrrhotite may or may not possess magnetic properties, which in turn influences the reactivity of the mineral surface to become oxidized. Becker (2009) elucidates that magnetic pyrrhotite is very reactive; forming ferric hydroxides as a result of rapid oxidation when the magnetic pyrrhotite surface is exposed to atmospheric conditions in flotation tanks or when deposited in tailing impoundments. The non-magnetic pyrrhotite is less reactive, suggesting low oxygen uptake, and lesser chances of the mineral to suffer oxidation layering. The common industrial practice where processed streams are deposited as composite tailing in dams from all processed streams (Hay 2005; Rule et al., 2008; Amponsah-Dacosta 2017) most likely defeats the ideal of distinguishing the different pyrrhotite types prior to re-treating dormant or already deposited tailings. Therefore, when re-treating historic deposited tailing, the pyrrhotite-associated material could be most likely expected to be affected by surface layering.

4.1.3.4.4. Slime coating. Hydrophilic minerals (silicates and chromite spinels) and phyllosilicate ultrafine particles (produced during grinding) coat the valuable mineral surfaces thereby hindering their floatability (Grano et al., 2004; Nel et al., 2005; Molifie 2021). Poor fines/ultrafine value recovery may be attributed to inhibited collector adsorption and minimal bubble-particle contact at the mineral surface (Singh, 2016; Ross et al., 2019; Molifie 2021). Operating in an open circuit ball milling or inert stirred milling configurations are reported to minimize the influence of surface slime coating by producing a narrower size range in an effort to reduce value rejection to the tailing; as well as reclaiming values from tailing (Buys et al., 2004; Nel et al., 2005; Whitworth et al., 2022). Molifie (2021) emphasizes that the phyllosilicates present in the flotation pulp do not only coat the fine/ultrafine valuable minerals hindering recovery but also cause imbalances in the pulp rheology and froth stability affecting gas dispersion for bubble-particle interaction. Water/pulp chemistry is also reported to affect fines/ultrafine mineral surfaces by coating the surfaces as a result of ions in solution riming the mineral surface (Pease et al., 2006).

4.1.4. Approaches to mitigating value losses to tailings

Finer particle liberation is of interest to improve value recovery from coarse particles reporting to the tailing as incomplete/partially liberated grains; however, fine grinding produces slime, which has been a challenge in grinding circuits. Over the last decade and a half, several studies in various campaigns have explored alternative solutions to some extent to mitigate the challenges faced with value mineral rejection to tailing. The introduction of stirred milling has facilitated a finer grind with the ability to reduce fines production via grinding at narrow size fractions as well as to create active surfaces via attrition removing passivation/coating layers that engulf the already ground particles (Buys et al., 2004; Greet, 2009; Rule 2010, 2011; Rule and Schouwstra 2012; Whitworth et al., 2022). This development has enhanced value recovery in both main grinding circuits and ultrafine cleaner/recleaner flotation circuits. The latter targets improving grade concentration in primary and tertiary re-treatment scavenging circuits. More so, particle-bubble contact efficiency has been a concern in recovering value from the fine/ultrafine fraction – which eventually are rejected to tailings. Corin et al. (2021) outlined investigations that have explored optimising bubble size to enhance recovery and at the same time, attaining selectivity. Pease et al. (2006) suggest that fines do not require longer residence time or larger volumes of reagent for maximum recovery. The authors suggest that a detailed understanding of the particle size liberation characteristics of material being concentrated as well as the water and mineral surface chemistry are important parameters to consider. Pease et al. (2006) designed a stage-wise grind-float circuit using the characteristics and properties of these parameters to improve recovery, where each stage targeted a selected particle size (i.e. size in decreasing order) to avoid fines generation. In these circuits, grinding was achieved via inert grinding media stirred mills (i.e. IsaMills) followed by the use of conventional flotation cells. This size-by-size staged grind-float configuration proved effective in alleviating fine recovery problem at plant scale (Pease et al., 2006). For flotation performance in fine/ultrafine particles, Rule et al. (2008) and Hay (2010) – investigating at plant scale – have proven the use of column flotation to maximize recovery and improve concentrate grade in the cleaner circuits of a primary plant and a tertiary tailing re-treatment plant, respectively. In a plant-based case study, Sema et al. (2022) investigated the use of magnetic coagulation/agglomeration of fines/ultrafines to improve value mineral recovery from the secondary mill-float-mill-float (MF2) stream and final tailing slurry. Elsewhere, selective aggregation of fines via flocculation (Forbes, 2011; Ng et al., 2017) and fines agglomeration (Cheng et al., 2020) have been attempted and reported to be promising.

Even after addressing the problem of fine grinding for adequate liberation, loose PGM grains (<5 μm) are lost to the ultrafine tailing because conventional flotation shows limited recovery of ultrafine grains - tending to report to the slime fraction of the pulp (Singh, 2016; Ross et al., 2019). In a tailing re-treatment attempt to recover values from fines/ultrafine fraction, Singh (2016) and Ross et al. (2019) introduced the use of a hydrodynamic cavitation device (HCD), which significantly improves value recovery from fine/ultrafine particles. Notwithstanding, Ross et al. (2019) found that the effective application of the device to attain maximum recovery is to maintain the specified/optimum predetermined number of passes to avoid the effect of slime coating resurfacing on the mineral. They further suggested that the use of an effective dispersant would improve flotation should sliming recur. Attrition through intense mixing in pumping systems is known to remove the surface coating to some extent (Rule et al., 2008). Recent studies by Molifie (2021) have shown the use of sodium metasilicate to simultaneously serve as pulp rheology modifier, dispersant, and depressant to counteract adverse surface coating and high pulp viscosity by phyllosilicates in PGM and BMS flotation recovery from near-surface altered ores. As outlined earlier, plant instability (stops/start-ups) is one factor responsible for value rejection to tailings. Rule et al. (2008) in a pilot investigation found that at stable primary plant operation, tertiary tailing re-treat flotation recovery from the primary plant tailing stream yields an average of about 10% value recovery; while at unstable plant operations, the tertiary re-treatment flotation recovery reaches about 25% relative to the tertiary plant feed. The latter becomes imminent because more value material escapes in the tailings at unstable plant operations. Proffering an almost obvious solution, Rule et al. (2008) reported that maintaining stable plant operation significantly minimizes value losses to the tailing - a solution alluded by Rule and Anyimadu (2007).

5. Existing Low-grade platinum group mineral ore AND flotation tailing Re-treatment processes

Tailing re-treatment is viewed as mineral conservation with the global emergence of the idea of a circular economy and can be harnessed with economically efficient techniques or approaches. The high cost and energy requirements in the PGM primary metallurgical circuit suggest the need for alternative routes for tailings re-treatment, especially for the complex polymetallic PGE flotation tailings with inherent low-value grade. However, the large tonnage of the secondary resource from processed (as well as scavenging flotation re-processed) streams suggests still significant value to be recovered. The re-treatment of PGM metallurgical plant tailings via tertiary scavenging flotation began in the South African PGM industry in the early 21st century and has since gained increasing interest (Buys et al., 2004; Rule et al., 2008; Rule and Schouwstra 2012). The characteristic flowsheet for the re-treatment of the BIC flotation tailings (i.e. fresh online and dormant tailing materials) includes gravity and/or magnetic separation, cyclone classification, regrinding by ball mill and/or stirred mill (in bypasses), followed by tertiary scavenging concentrators. The tertiary flotation circuit typically includes rougher, cleaner, and recleaner banks (Rule and Schouwstra 2012; Little 2016; Letseli et al., 2018; Eastplats 2022). Re-treatment circuit configurations vary among operations depending primarily on the parent reef-type mineral composition from which the tailing originates (Buys et al., 2004; Rule et al., 2008; Northam AR 2017; Eastplats 2022). The UG2 chromitite BIC horizon contains chromite that can be recovered from the UG2 tailings for the production of ferrochrome via gravity concentration and subsequent PGM recovery in scavenging flotation circuits (Dawson 2010; Eastplat 2022). Most re-treatment plants follow the simplified block configuration in Fig. 7 - processing tailing materials from the MF2 circuit in a chrome concentrator followed by the PGM scavenging flotation treatment, then rejecting the final tailings to impoundments. The chromite recovery process precedes the tertiary flotation stage as a form of pre-treatment (Little 2016; Setlhabi et al., 2019; Impala RR 2021; Northam RR 2021; Sibanye Stillwater RR 2021); however, of specific note, even after the chromite recovery stage, the scavenging flotation feed still has high chromite composition (Little 2016). Unlike the re-treatment of UG2 tailings or chromite containing tailings, the Merensky Reef tailings re-treatment circuits have no preceding gravity concentration; the hydraulically mined materials from legacy TSFs are sent directly to tertiary ball mill grinding and scavenging flotation circuits (Buys et al., 2004; Rule et al., 2008).

Gravity and magnetic concentration are two primary techniques used in processing ferrochrome materials - i.e. chrome ores or PGM-chromite containing tailings – in the BIC (Setlhabi et al., 2019; Sahu et al., 2021; Sylvania AR, 2021; Eastplat 2022; Whitworth et al., 2022). Spirals are gravity concentration technology known to be effective and well established as the main beneficiation method for chromite recovery (Von Gruenewaldt and Hatton 1987; Gu and Wills 1988; Dawson 2010; Murthy et al., 2011; Engelbrecht 2012; Maharaj et al., 2012; Russell 2020; Molefe and Baloyi 2022). Gravity spiral separation takes advantage of the chromite relative density (4.1 – 5.1) within similar size range for effective separation from the residual BIC crushed rock silicate matrix containing orthopyroxene (3.2 – 3.5), plagioclase (2.6), Mg-olivine (3.2), clinopyroxene (3.2 – 3.5) (Gu and Wills 1988; Molefe and Baloyi 2022). PGM grades in ferrochromite spiral processed tailings average 1 – 4 g/t PGE (Von Gruenewaldt and Hatton 1987; Rule 2010; Aquarius AR, 2010 – 2011; Molefe and Baloyi 2022). Although the PGMs were not targeted in the ferrochromite primary process, the upper limits of the reported PGE content in the ferrochromite spiral tailings appears high for these tailing materials.

Magnetic separation and/or aggregation is another physical treatment technique that is often used in the concentration of PGM and chromite containing materials as well as for gold and copper sulfide ores in various applications (Rosenblum et al., 1986; Churchill and Lumsden 2007; Rabatho et al., 2010; Wood et al., 2012; Letseli et al., 2018; Eastplats 2022). Quite recently, Anglo American Platinum investigated a magnetic coagulation conditioning technique at its Mogalakwena metallurgical plant by inducing magnetism in the secondary MF2 slurry stream to enhance PGM recovery in the fine and ultrafine particle fraction (Sema et al., 2022). The nine-month plant test campaign showed improved Pt recovery of 0.97% (relative to the overall individual Pt recovery) where Pt alloys and ferro-platinum minerals in the < 10 μm ultrafine particle fraction were the target for the magnetic pre-conditioning. The selective magnetic coagulation achieved an overall plant PGE recovery increase of 0.64% with a greater influence on the Pt species than the Pd ones. In other magnetic separation applications, Letseli et al. (2018) demonstrated the application of wet high intensity magnetic separation (WHIMS) and low intensity magnetic separation

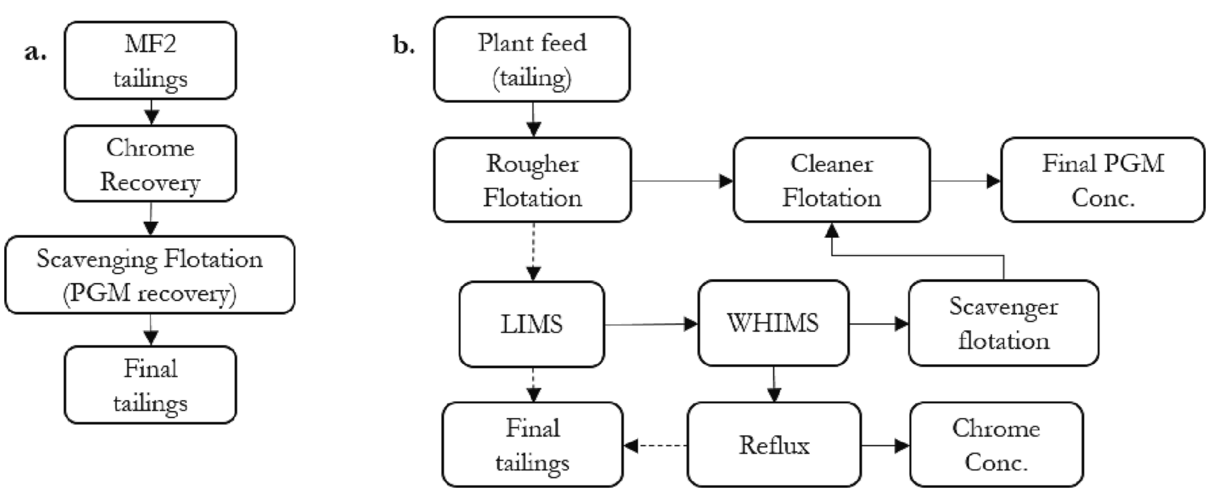

Fig. 7. (a) Simplified typical block flowsheet diagram from industrial platinum group mineral tailing re-treatment circuits. (b) Block flowsheet of a chromite-platinum group mineral tailing re-treatment process. Modified after Letseli et al. (2018). LIMS stands for low intensity magnetic separation and WHIMS, wet high intensity magnetic separation.

(LIMS) in a pilot campaign on a highly weathered UG2 material from the chromite tailings rougher flotation stage. The ferrous rejects were ultimately disposed, while the chromite containing PGM materials were further conditioned prior to scavenging flotation and final tailing deposition (Fig. 7). Rabatho et al. (2010), in a lab scale investigation, demonstrated the application of dry magnetic separation to recover 2E PGEs from a mixed UG2-Merensky flotation tailings material. Pt (0.7 g/t) and Pd (0.2 g/t) were upgraded in the magnetic product to 42 g/t and 13 g/t respectively. Their work shows that the PGMs were mainly recovered from the chrome containing spinel ($MgCr_2O_4$). In an investigation to recover chromite from PGM tailings, Setlhabi et al. (2019) evaluated the efficiencies of magnetic and advanced gravity separation techniques. They found that both techniques showed improved recovery efficiencies of chromite in the coarser fraction (>75 μm) obtained from the cyclone underflow. Moreover, the advanced Falcon gravity separation was observed to be efficient at > 45 μm size fraction – recovering fine particles that could not be recovered with the spiral separator. The work by Setlhabi et al. (2019) provided additional evidence that when upgrading PGM tailings using these techniques, particle size influences the re-treatment process, primarily gravity separation. This argument is also alluded to by other studies (Güney et al., 2001; Wills and Napier-Munn 2006; Sema et al., 2022; Whitworth et al., 2022).

5.1. *Industrial platinum group mineral flotation tailing and chromite tailing re-treatment applications*

Interest in the re-treatment of both fresh online tailing streams and historic legacy tailing facilities have seen rapid growth in the context of BIC ore processing. Sibanye Stillwater, Impala Platinum, Northam Platinum, and Eastplats are among the major South African PGM producers that have industrialized PGM valorisation from dormant PGM flotation tailings and online fresh tailing streams, as well as re-treating chromite tailings. Chrome is extracted from the UG2 concentrator tailings at Sibanye Stillwater's chrome re-treatment plant (CRP) at the Rustenburg Kroondal and Marikana operations (Sibanye Stillwater RR 2021). Sibanye Stillwater own a number of tailing re-treatment operations including the Western Limb Tailings Re-treatment (WLTR), BTT, Eastern Tailings Re-treatment (ETTP), and Platinum Mile. Anglo American Platinum commissioned the first PGM tailing re-treatment plant in the early 2000 s at the WLRT facility near Rustenburg – now owned by Sibanye Stillwater – for the re-treatment and recovery of PGM from legacy Merensky processed tailings (Buys et al., 2004; Rule and Schouwstra 2012). The WLTR flowsheet includes hydromining (recovering tailings by high-pressure water mining), ball milling, rougher flotation, rougher concentrate IsaMill regrinding, and cleaner/recleaner flotation (Fig. 8). The IsaMill technology was proven on a pilot scale and later introduced in the WLRT circuit for the regrinding of the cleaner/recleaner circuits feed to upgrade the tertiary rougher flotation concentrate to smeltable concentrate grades (Buys et al., 2004; Rule and Schouwstra 2012). The inert grinding media environment of the stirred mill reportedly does not only improve the valuable mineral liberation, but also removes the oxidized iron layers from the particle surfaces of these minerals, thereby improving the value metal recovery (Whitworth et al., 2022). Flotation rejects from the rougher and cleaner circuits in the WLRT configuration constitute the final tailings. The plant was operated by Anglo American Platinum up until 2016 when the Rustenburg platinum operations were taken over by Sibanye Stillwater (Sibanye Stillwater RR 2017).

The BTT facility re-treats and recovers chromite and PGMs from the Marikana operation TSF. This project was commissioned by Lonmin in February 2018, and was later acquired by Sibanye Stillwater (Sibanye Stillwater RR 2021). Tailing streams emanating from the MF2 primary UG2 circuits in the Marikana operation pass via a chrome recovery circuit using gravity spiral concentrators and are re-treated at the Eastern Tailings Re-treatment (ETTP) operation via tertiary mill-float circuit. The tertiary milling is achieved through an open circuit containing ball mill and IsaMill prior to a tertiary scavenging flotation circuit (Fig. 8; Little 2016; Little et al., 2017). The Platinum Mile re-treatment operation located in Rustenburg adjacent to the Paardekraal TSF recovers PGMs from tailing streams of the Rustenburg Waterval and Retrofit concentrator plants (Rule et al., 2008; Sibanye Stillwater RR 2021). The re-treatment operation uses vertical stirred mills in their PGM tailing recovery circuit where the concentrates from the cleaner/recleaner circuits are at acceptable grades that are processed in the downstream smelters (Rule 2010). The feed to the Platinum Mile PGM tailing re-treatment plant is < 1 g/t producing a recovery ranging from 9 to12.5% at a grade range of 80 – 100 g/t (Rule 2010; Sibanye Stillwater RR 2016 – 2021). Platinum Mile treats two separate streams – i.e. the UG2 concentrator stream and the UG2–Merensky mixed stream: via scavenger flotation. The Platinum Mile Merensky re-treatment circuit is similar to the WLRT configuration; however, ultrafine regrinding is achieved with a SMD vertical stirred mill. Ultrafine grinding using stirred milling technology is reported to effectively address plant challenges associated with incomplete liberation and selectivity, thereby improving concentrate grade and metal recovery (Rule et al., 2008). More so, the use of column flotation has proven to be ideal and very effective for value recovery and successfully rejecting of chromite as a result of the deep froth bed the column cells maintain when processing finely ground UG2 materials containing a high presence of chromite (Minnaar et al., 2005; Hay 2010). At its re-treatment plant, the Platinum Mile operations commissioned the column flotation technology in 2008 in the recleaning circuit of its Merensky and UG2 streams and has since achieved improved PGM recovery from the ultrafine particle fraction (Rule et al., 2008; Sibanye Stillwater RR 2021).

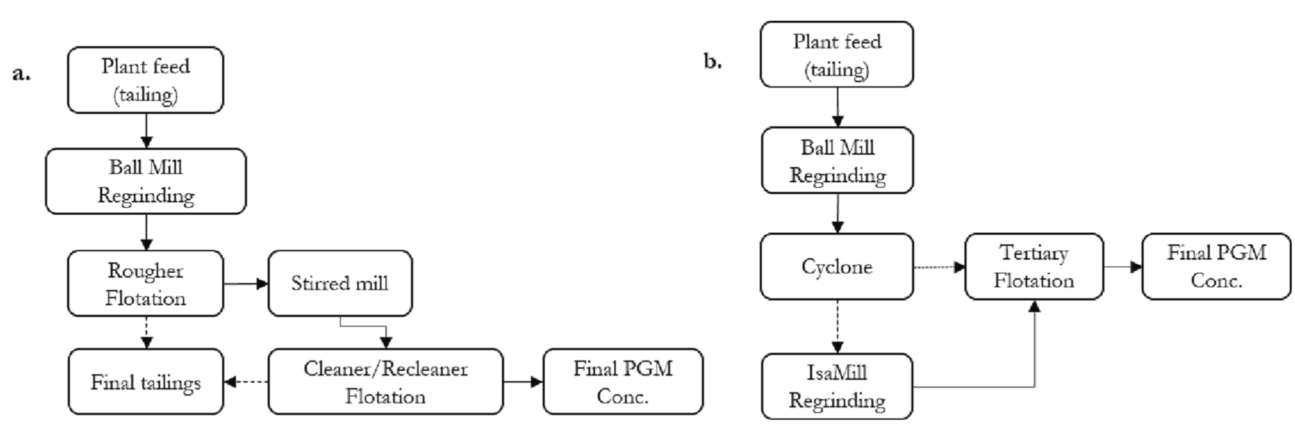

Fig. 8. (a) Simplified block diagram of the Western Limb Re-treatment facility: dashed lines indicate tailing stream, line indicate slurry/residual stream.(b) Simplified block diagram of Eastern Tailings Re-treatment (ETTP); dashes - underflow, dots - overflow, line – streamflow.

Impala Platinum has a flotation tailings re-treatment tertiary scavenging plant, re-treating fresh tailing materials from its high-grade and low-grade primary plant streams prior to the final deposition in the TSF. The feed size distribution entering the high and low grade secondary rougher flotation circuits from the primary plant have a particle distribution of 59% passing 75 μm and 65.4% passing 75 μm respectively, indicative of a relatively coarse distribution that subsequently enters the tertiary scavenging plant (Hay and Schroeder 2005). According to the Impala Platinum 2021 mineral resource and ore reserve report, the Impala Merensky primary plant achieves recoveries as high as 89 – 91% in the Merensky circuit and at the same time attains 79 – 81% recovery in the more complex UG2 circuit (Impala RR 2021). The primary plants overall recoveries are reportedly enhanced by recovery from the tailing scavenging circuits re-treating tails from both the UG2 and Merensky plants. Typical to other re-treatment circuits, Impala UG2 tailing flotation scavenging circuit re-treats the tailings through a chromite recovery plant prior to the tertiary flotation stage. According to the Impala RR (2021) report, the company has also reached a decision to reprocess its historic dormant tailing storage facilities – i.e. TSF1 and TSF2 – following mineral resource estimation studies and trial mining operations.

Northam Platinum re-treats its tailings at the Eland and Booysendal operations. Since 2015, the Northam Eland mine has been on care and maintenance; however, the metallurgical plant was recommissioned in 2020 for the reprocessing of the tailings for chromite and unrecovered PGMs (Northam AR 2020). Northam Platinum also operates the Booysendal South Tailings re-treatment project targeting the processing of about 8.7 Mt of flotation tailings for chromite and PGMs. Feed from the TSFs are mined via hydromining and sent through chrome spiral concentrators followed by scavenging flotation for PGM recovery and final rejection of the residual material (Northam RR 2021).

Eastplats re-treats the Zandfontein historic UG2 tailings at the Crocodile River Mine (CRM) for chrome and PGM. The re-treatment plant production from December 2020 to February 2022 showed that recovery was about ~ 11% of the tailings head grade (Eastplats 2022). The Eastplat TSFs reclamation project employs hydraulic mining (high-pressure water jet mechanism) and may include mechanical loading for bonded layered coarser materials. The hydraulic actions primarily erode the deposited tailings and the water-jetted slurry is collected in sumps and pumped through pipelines to the re-treatment plant. The mechanically excavated material is transported via trucks and screened, followed by regrinding at the mill circuit and combined with those piped from the hydraulically mined re-treatment feed. The tailings emanating from the legacy TSF are processed via wet high intensity magnetic (WHIM) separation for chrome (Fig. 9) while tailing materials from the existing primary plant flotation circuits are processed via gravity spirals prior to the scavenging flotation circuits, achieving 6E PGE grade of about 60 – 80 g/t in the presence of ~ 3.5% chrome (Fig. 10). Eastplats (2021) reports that the magnetic separation yielded superior results compared to the gravity spiral technique in concentrating chrome from the tailings. Of specific note, Eastplats operates the only large-scale magnetic separation re-treatment plant in South Africa.

Sylvania Platinum Ltd also known as Sylvania Dump Operations (SDO) is a chrome tailings re-treatment company operating in both the Eastern and Western Limbs of the BIC (Sylvania AR 2021). SDO reprocesses fresh online and historical chrome tailings at six chrome re-treatment plants producing chrome and PGM concentrates. SDO employs grinding, gravity spiral concentration, WHIM separation, and MF2 (fine grinding) in varying circuit configurations at its operations. Crushing and heavy medium separation (HMS) are additional process stages used in plants where ROM mineral waste are treated. Table 7 presents a summary of SDO operations and re-treatment circuits. SDO reports that the combined operations PGM recovery efficiency range from 52 to 55%, where the overall recovery value is influenced by each individual plant feed material and circuit configuration.

In other commercial industrial PGM re-treatment applications, circuit configurations involve the high shear hydrodynamic cavitation Mach Reactor instead of ball mill grinding. Nevertheless, the re-treatment circuit is also followed by tertiary flotation that may have ultrafine grinding in the cleaner circuits (Ross et al., 2019; Singh, 2016). With successful pilot scale studies, HCD have found application in the PGM industry where two industrial re-treatment tailing operations in

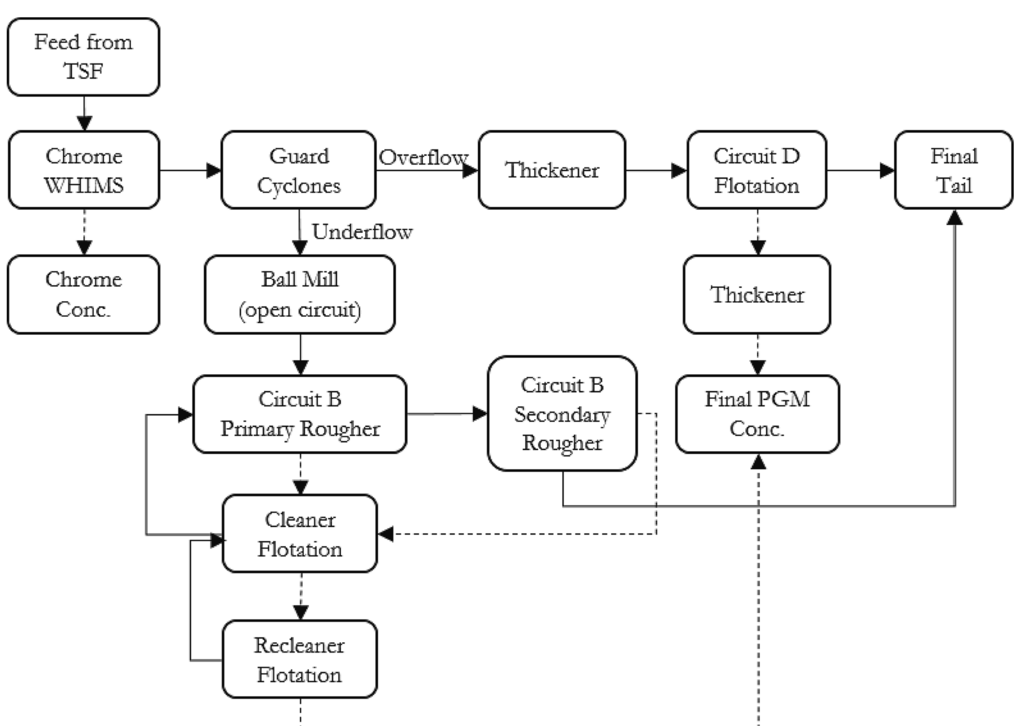

Fig. 9. Eastplat recommissioned Zandfontein re-treatment plant block flowsheet highlighting recovery through circuit B and circuit D; dashes – concentrate streams and line – slurry/residual stream.

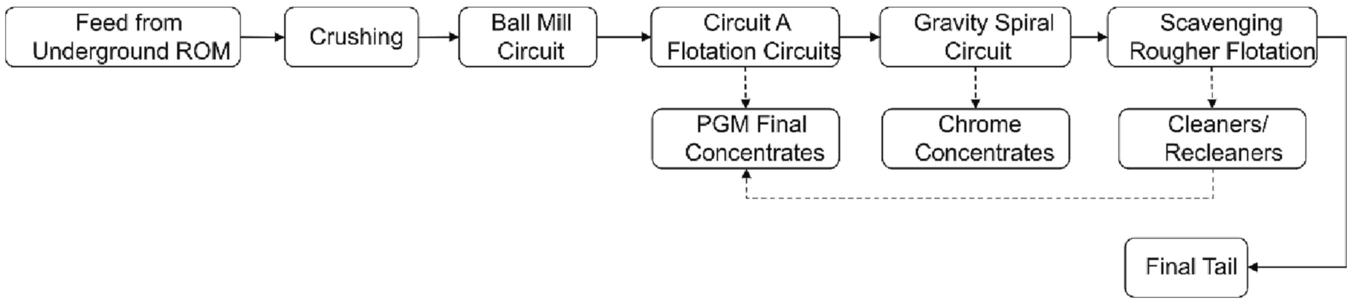

Fig. 10. Eastplat existing platinum group mineral re-treatment block flowsheet highlighting recovery from the primary plant fresh online tailing stream; dashes – concentrate streams and line – main/residual stream.

Table 7
Tailing re-treatment circuit configurations of Sylvania Platinum Ltd operations in the Bushveld Igneous Complex.

Operation	Feed Material	Treatment Process Configuration	Production Capacity (ktpm)	Year of First Operation
Millsell	Tailing dumps and fresh tailings	Mill, Spiral, WHIMS, MF2	25	2008
Mooinooi	ROM, Tailings dumps and fresh tailings	Crush, Mill, HMS, Mill, Spiral, WHIMS, MF2	60	2012
Lesedi	Tailings dumps	–	35	2011 (acquired 2018)
Doornbosch	Tailings dumps and fresh tailings	Mill, Spiral, WHIMS, MF2	25	2011
Lannex	Tailings dumps and fresh tailings	Mill, Spiral, WHIMS, MF2	36	2009
Tweefontein	Tailings dumps and fresh tailings	Mill, Spiral, WHIMS, MF2	42	2012

the BIC western limb are reportedly using this technology on a mixed UG2-Merensky tailings (Ross et al., 2019). The technique has also been evaluated in bench scale campaigns on PGM-bearing ores (Singh et al., 2022). An advantage of the HCD is the high shear attrition impact and energy dissipation on the tailing material. Such mechanisms activate the value mineral surfaces by physical removal of oxidized layers and slime coatings resulting in improved surface exposure and improved grade-recovery relationship. During flotation, the collection mechanism is enhanced via nano-bubble formation which targets fine and ultrafine value particles (Ross et al., 2019; Singh et al., 2022). Furthermore, while simultaneously cleaning the valuable mineral surfaces, the mechanisms operating in the reactor are known to also aid in depressing the gangue minerals while at the same time improving value mineral flotation kinetics – most specifically in the fine and ultrafine particle fraction (Singh, 2016; Ross et al., 2019; Singh et al., 2022). Singh (2016) reported the industrial tailing re-treatment final recovery and grade to be ~ 30 % and 20 – 30 g/t of the tailing feed – i.e. without regrinding in the circuit. As it is with other re-treatment operations, current industrial re-treatment processes involving hydrodynamic cavitation produce concentrates for direct processing through the cost and energy intensive smelting and conversion unit stages.

5.2. Other potential pre-treatment and extraction routes

Unlike flotation separation governed by mineral surface properties, leaching requires only partial liberation or surface exposure of the metal for the lixiviant to access and extract the targeted mineral value (Lottering et al., 2008). An exception occurs when the metal is chemically inert to the lixiviant, thereby rendering the metal exposure pointless. One main advantage of the hydrometallurgical leaching route is that it aims directly at PGM extraction rather than making concentrate as in flotation separation. In a heap leaching pre-treatment application with the use of microbial attack on low-grade PGM Platreef ore, Mwase et al. (2014) observed that the bioleaching of the coarsely crushed low-grade ore assisted in recovering the base metal sulfides but at the same time dissolved the acid consuming gangue minerals. Microbially assisted biooxidation has been proposed in other PGM and gold/silver precious metal tailing re-treatment investigations (Das, 2010; Maes et al., 2016, 2017; Cecchi et al., 2017).

What is very important to consider in leaching pre-treatment of PGM sulfide bearing ore or tailings materials is the complete oxidation of the sulfides, which is known to play a cardinal role in the PGM extraction from engulfed sulfides and gangue phases for the subsequent precious metal dissolution stage (Safarzadeh et al., 2018). However, incomplete sulfide oxidation results in the formation of intermediate sulfur species in the dissolution system. Incomplete sulfur oxidation is a major challenge when using acidic (bioleaching or pressure oxidation leaching) environment as PGM pre-treatment for low-grade or tailing material; where these formed intermediate species and become detrimental in subsequent downstream processes thereby hindering precious metal leaching and recovery (Liddell and Adams 2012; Mwase 2016; Mwase and Petersen 2017; Shaik and Petersen 2017).

The re-treatment of copper tailings in studies elsewhere investigated synergistic ammoniacal leaching and ammonia-bacteria assisted alkaline leaching toward selective BMS dissolution (Yin et al., 2018; Turan et al., 2020). Ammoniacal leaching treatment has been also investigated on low-grade PGM Platreef ores to achieve selective BMS extraction (Petersen et al., 2013; Muzawazi and Petersen 2015). In the hydrometallurgical processing of PGM bearing materials (ores, low-grade concentrates, and tailings), bioleaching, pressure oxidation followed by thermal treatment, and ammonia leaching are pre-treatments to only dissolve the BMS. To date, no investigations have been reported in the literature on direct hydrometallurgical extraction of PGEs from PGM flotation processed tailings. Nevertheless, studies have shown the direct leaching of PGEs from low-grade PGM bearing ores in cyanide medium (Mwase et al., 2014; Mwase 2016). Mwase's heap leaching studies on the direct cyanidation of the low-grade PGM ore material showed promising PGE extraction efficiencies (i.e. ~ 57.8% Pt, 99.7% Pd, and 90.3% Au recoveries), however, at the trade-off of long extraction times (>300 days). Prominent in the literature are hydrometallurgical investigations toward extraction dissolution of low or very low-grade PGE flotation concentrates in chloride/chlorine gas (HCl/Cl_2) as well as cyanide media (Green et al., 2004, Adams et al., 2011; Liddell and Adams

2012; Mwase et al., 2012; Shaik and Petersen 2017). Unlike the direct leaching of PGM ores as in Mwase's studies, the HCl/Cl_2 hydrometallurgical route has shorter residence time but is highly cost intensive: limiting the HCl/Cl_2 dissolution system to flotation concentrates and downstream refining processes.

Mohamed et al. (2016), in an attempt to re-treat PGM tailings from Two Rivers platinum operations, evaluated the use of thermochemical pre-treatment at 550 °C with ammonium sulfate. The thermochemical step was followed by dissolution in aqueous media to induce liberation by releasing major gangue elements in solution. The thermochemical-treated residues that had formed water-soluble minerals were further leached in ultra-pure water and nitric acid solution (0.63 M at 25 – 95 °C) in the aqueous dissolution stage. Extraction efficiencies for the major elements were 25% magnesium, ca. 60% aluminium, 27% chromium, ca 80% calcium, 35% iron, and 32% silicon. On analyses of Table 8 generated from the studies by Mohamed et al. (2016, 2017), not all the gangue minerals heavily relied on the thermochemical phase to become disintegrated in the gangue minerals structure for subsequent dissolution. In another approach of the same study, Mohamed et al. (2016, 2017) investigated acid leaching (at similar experimental conditions) prior to the thermochemical pre-treatment phase. Their work showed that the acidic phase had an appreciable influence on the silicon and calcium extraction; while chromium and iron extractions were mainly contributed by the thermochemical phase. Aluminium and magnesium extractions showed that both the thermochemical and acid leaching steps contributed to their final dissolution extraction. Although the study did not provide any information on the PGM concentration before and after the pre-treatment process, the magnesium (25%) extraction efficiencies in this study were substantial compared to the magnesium extraction in other studies that had used BIC tailing materials (Meyer et al., 2014). Despite the use of a low-cost, recyclable reagent – ammonium sulfate – that was effective in the thermochemical (i.e. first step) pre-treatment stage, it is important to mention that the thermochemical step would be a highly energy intensive step.

Mineral carbonation of BIC tailings has been evaluated, suggesting the dissolution of magnesium species in the tailings as a potential pre-treatment stage toward valorising the PGM tailings (Vogeli et al., 2011; Meyer et al., 2014; Ncongwane et al., 2018). The targeted mineral species for carbonation is magnesium – sourced from olivine and its altered species, primarily serpentine (Wang and Moroto-Valer 2011, 2013; Sanna et al., 2014). However, the major magnesium gangue phase in the BIC tailings is the pyroxene group (mainly enstatite) and it has proven to be less than ideal as the pyroxenes are more refractory to dissolution, achieving only 3.3 – 20% maximum dissolution for the BIC tailings (Vogeli 2012; Meyer et al., 2014) and 30% maximum dissolution in another study (Sanna et al., 2014). Moreover, the mineral dissolution phase of the carbon sequestration process is not only challenged by the poor major element dissolution when using the BIC tailings, but also the increasing cost for large volumes of reagents the process generally demands for pH swing, requiring neutralisation and washing stages (Wang and Maroto-Valer, 2011), as well as the low concentration of the altered mineral species in the BIC ore bodies (Table 3). These factors along with the limited liberation achieved through the gangue disintegration via dissolution limits the viability the process in the context of BIC tailings (Vogeli 2012; Meyer et al., 2014). Notwithstanding, successes attained with altered serpentine elsewhere (Wang and Moroto-Valer 2011, 2013; Sanna et al., 2014) has yet to be evaluated on BIC tailings from weathered/oxidized near-surface sources. BIC tailings that may contain substantial composition of olivine and its alteration species could in principle ideally serve an alternative pre-treatment route for valorising such oxidized originated tailing materials. From these studies (Yoo, et al., 2009; Teir et al., 2007a, 2007b; Wang and Moroto-Valer 2011, 2013; Sanna et al., 2014; Meyer et al., 2014), it is quite established that olivine and serpentine are the most favoured minerals for magnesium extraction in the carbonation process, while orthopyroxenes and plagioclases have proven less reactive to favour dissolution for carbonation.

Table 8
Contributing effect of acidic leaching before and after thermochemical pre-treatment on Two River tailings (Mohamed et al., 2016, 2017).

Major Element	Acid leach before the thermochemical stage	Acid leach after the thermochemical stage	Contributing stage
Calcium (Ca)	69.0 ± 1.6%	80.0 ± 3.6%	Acid (before)
Silicon (Si)	29.9 ± 1.4%	30.5 ± 1.2%	Acid (before)
Aluminium (Al)	27.0 ± 0.7%	59.1 ± 0.5%	Both stages
Magnesium (Mg)	9.1 ± 0.0%	25.2 ± 1.0%	Both stages
Chromium (Cr)	0.1 ± 0.0%	26.9 ± 1.3%	Thermochemical
Iron (Fe)	2.9 ± 0.0%	34.7 ± 1.2%	Thermochemical

6. Value significance in platinum group mineral flotation tailings

South Africa remains the world's second largest producer of palladium and the top producer of all the other PGMs, possessing about 90% (63,000 t) of the known PGM reserve (70,000 t) in the world (USGS 2022). The current primary production and economic reserve provide extensive evidence of the paramount role the South African PGM industry plays in sustaining the global supply of the commodity (Johnson Matthey 2022; USGS 2022). Consequently, the larger the supply volume of the precious minerals from its primary sources through mining and concentration processes, the more tailing materials that would be generated from processed streams. Reviewing the mineral resource and ore reserve reports of selected major PGM producing companies in South Africa, Fig. 11 shows the ore reserve trend (i.e. excluding resources) and the combined reserve 4E PGM grade trend in the last decade. The South African PGM concentrators are known to experience residual value losses of about ~ 10 – 20% of the 4 – 5 g/t 6E PGM plant head grade; these losses tend to be however lower in highly optimized circuits (Hay 2010; Rule and Schouwstra 2012; Ndlovu 2015; Rose 2016; Sinisalo and Lundström 2018). The plant milled head grade in recent years tended toward the range 3 – 4 g/t 4E/6E PGM (Fig. 11); while at the level of individual operations (i.e. for each major producer) this value may be in the range of 3.0 – 5.5 g/t 4E/6E (Table 9). This section of the review compiles selected company annual reports, which collate data of the overall managed active operations of each company - excluding projects. Some minor companies are not included in this review due to limited availability of company data.

6.1. Economic value potential in tailings from primary production

In the BIC MF2 circuit configurations, secondary rougher tailings may be channelled directly to the final tailing dam or in some operations to tertiary scavenging recovery plants (Hay and Schroeder 2005; Rose 2016; Little 2016; Sibanye Stillwater RR 2021). The latter is a growing trend in the South African PGM industry. According to Vogeli et al. (2011), the BIC PGM operations produce about 77 Mtpa of tailings. Compared to the compiled data reported for production performances from the selected major BIC PGM producing operations (i.e. from the primary metallurgical plant – excluding all surface tailing re-treatments), Vogeli et al. (2011) reported value remains well in range as depicted in Fig. 12. The average material processed annually is about 76 Mt at a 4E PGM tailing deposition grade that averages around 0.5 g/t (Fig. 12). The potential economic reserve compiled from the reviewed company annual reports shows a substantial resource base in primary concentrators tailings – containing about ~ 1.2 – 1.4 Moz (37.3 – 60.9 t) of 4E PGE value rejected to tailing streams annually (Fig. 13).

Highlighting a few operations, Anglo platinum's Klipfontein Central tailings dam was reported in 2004 to possess a resource potential

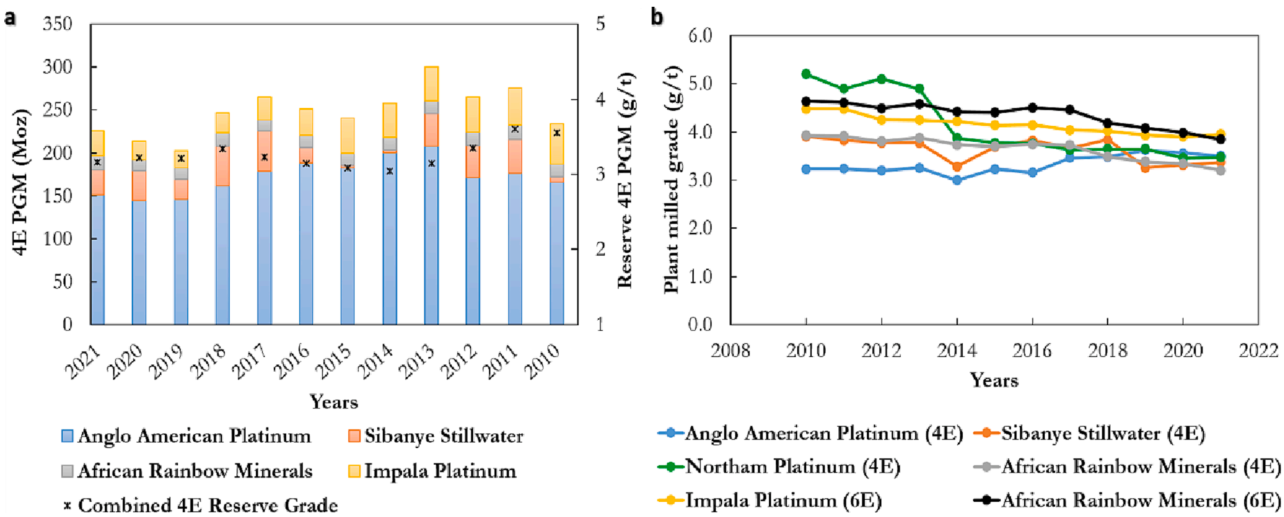

Fig. 11. (a) Bushveld Igneous Complex platinum group mineral 4E ore reserve and grade trend over a decade. (b) Concentrators milled head grade (4E/6E) at selected major producers. (African Rainbow Minerals AR, 2010 - 2021; Anglo Platinum AR, 2010 – 2021; Anglo Platinum RR, 2010 – 2021; Impala AR, 2010 - 2021; Impala RR, 2010 - 2021; Northam AR, 2010 - 2021; Northam RR, 2010 - 2021; Sibanye Stillwater RR, 2016-2021; Sibanye Stillwater AR, 2016-2021).

Table 9
List of selected primary platinum group mineral producing companies in South Africa reporting 4E/6E plant feed grade from 2017 to 2021.

Company Name	Managed Operations (ownership)	Source	2021	2020	2019	2018	2017
African Rainbow Minerals*	Two Rivers (54%)	UG	3.43	3.45	3.52	3.63	3.90
	Modikwa (41.5%)	"	4.51	4.82	4.92	4.98	5.43
Anglo American Platinum	Mogalakwena (100%)	Surface	3.23	3.32	3.45	3.2	3.09
	Amandelbult (100%)	UG and Surface	4.18	4.26	4.05	3.98	3.86
	Mototolo (100%)	UG	3.14	3.34	3.23	3.23	3.04
Impala Platinum*	Rustenburg (96%)	UG	4.05	3.91	3.99	4.09	4.06
	Marula (73.3%)	"	4.37	4.70	4.4	4.33	4.26
Northam Platinum	Eland (100%)	Surface	2.45	2.73	–	–	–
	Booysendal (100%)	UG	2.77	2.59	2.72	2.71	2.7
	Zondereinde (100%)	"	4.97	5.03	4.96	4.95	4.8
Sedibelo Platinum	Pilanesberg (100%)	Surface	1.42	1.79	1.57	1.69	1.45
Sibanye Stillwater	Rustenburg (74%)	UG	3.38	3.38	3.48	3.6	3.7
	Marikana (80.64%)	"	3.87	3.7	3.61	4.57	4.61
	Kroondal (50%)	"	2.4	2.46	2.46	2.48	2.42

* Grades are reported as 6E platinum group mineral; UG = (Underground).

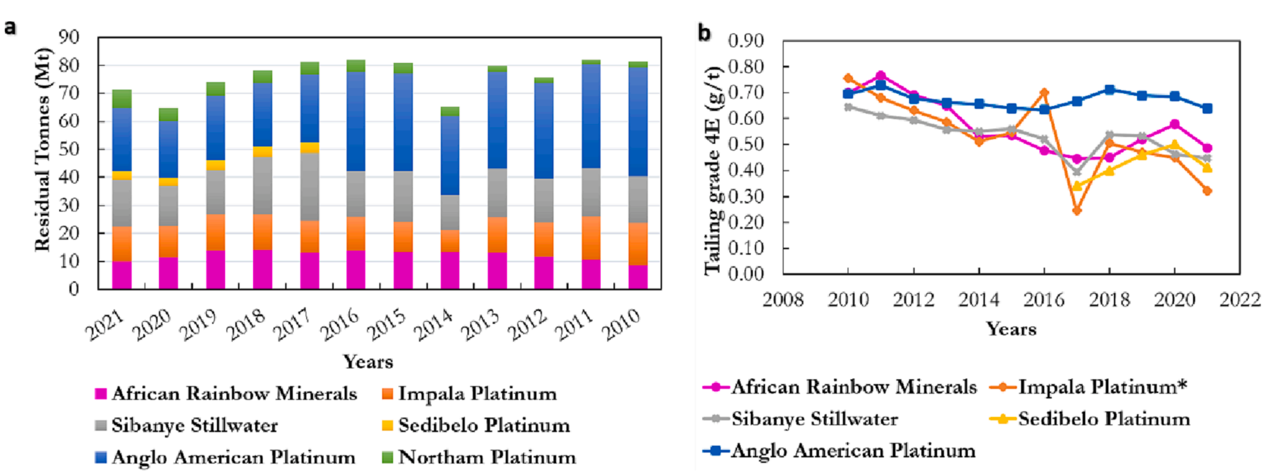

Fig. 12. (a) Annual residual milled tonnes produced from primary concentration processes at major South African platinum group mineral companies 2010–2021. (b) Trend of platinum group mineral tailing grade. * Impala tailing grade is reported as 6E.

calculated at 186 Mt containing 1.08 g/t PGE + Au. The resource was estimated to contain about 4 Moz of platinum or a combined 6E PGE content of 6.45 Moz (Buys et al., 2004). In 2008, Anglo American Platinum reported a cumulative amount of tailings generated from all its operations over the years to be 730.8 Mt (Anglo Platinum AR 2009). The historical tailing deportment at Amandelbult UG2 circuits ranged

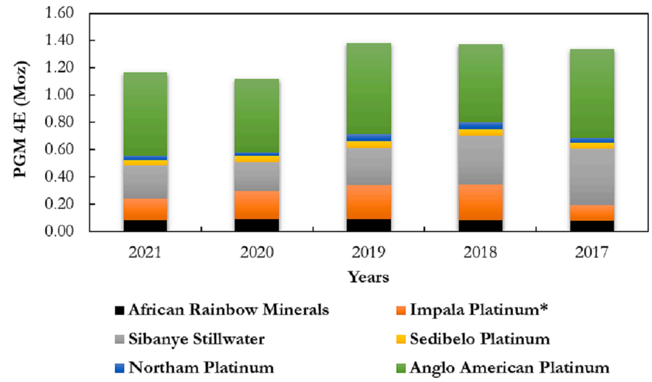

Fig. 13. Potential platinum group element value in tailings calculated from the average plant performance of major platinum group mineral producing companies report. * Impala value are 6E based.

between 0.8 and 1.0 g/t 4E PGE until late 2009 when the plant was optimised with the installation of stirred mills. After optimisation, the value rejection to tailings reportedly declined to a steady result at about 0.5 – 0.6 g/t 4E PGE – the plant target (Rule and Schouwstra 2012). According to Anglo American Platinum's interim reports (Anglo Platinum IR, 2010 – 2021), the company's overall operations performance in the three BIC reefs has been well within an average range of 0.5 – 0.7 g/t 4E PGE rejection to the tailings (Fig. 14). Moreover, data collated from all Anglo American Platinum's managed operations have cumulatively generated ~ 355.86 Mt of tailings in the reported period.

Hay (2010) investigated Northam's UG2 plant production performance for optimisation and reported concentrate recovery from July 2003 to April 2009 in the range 79 – 85%. The annual tailing deposition ranged 0.72 – 1.12 Mtpa at a 4E grade of 0.64 – 0.87 g/t. After the plant optimisation in April 2009, the concentrator achieved a recorded PGM recovery up to 88.4 % at an average throughput of about 96 ktpm. The throughput capacity was reported to have increased to 102 ktpm by September 2009. In 2017, Northam Platinum revealed in its annual report that the Booysendal South TSF contained about 8.7 Mt milled processed residue, and they were keen on re-mining and reprocessing the dam (Northam AR 2017). More recently in 2021, the company reported that re-treatment at its Booysendal and Eland TSFs had been commissioned to recover PGMs lost to tailings as well as chrome residues. Currently, Northam Platinum's overall operations produces residual annual tailing deposition of up to 6.62 Mt and 4E recovery ~ 90% (Northam AR 2021). An independent competent person's report on Eastern Platinum's Crocodile River decommissioned platinum mine reported that the TSF contains about 7.188 Mt deposited tailing material with a 4E PGM grade of 1.18 g/t (Eastplats 2022). The re-treatment operation at Eastplats was commissioned in December 2020 and has since been in production.

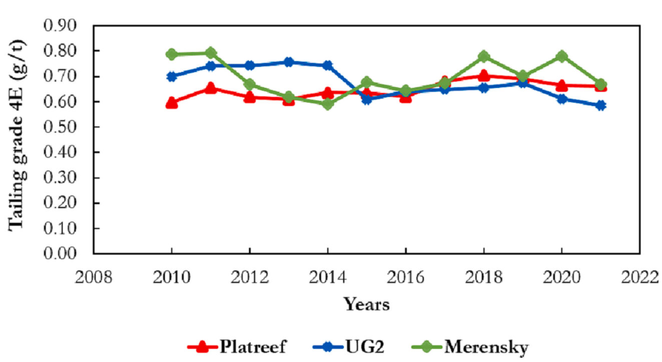

Fig. 14. Reported concentrator tailing grade of the three Bushveld reefs from all Anglo American Platinum operations in the period 2010 – 2021.

6.2. Economic value potential in re-treated tailing residue

PGM tailing re-treatment or tertiary scavenging flotation recovery produces about 9 – 12% average recovery of PGM value from fresh tailing streams emanating from stable plant operations and historical dams (Eastplats 2022; Aquarius AR 2010 – 2011; Sibanye Stillwater 2016 – 2021). Tailing re-treatment plants may achieve PGM recovery of 20 – 25% (of an average tailing head grade of about ~ 0.65 g/t 4E) and even up to 30 – 40% (of an average tailing head grade of about ~ 1.24 g/t 4E) of the re-treatment plant feed grade (Fig. 15). Rule and Anyimadu (2007) investigated and found that materials being discharged from fresh tailing streams with a relatively high re-treatment recovery (20 – 25%) would suggest less stable plant operations. Conversely, materials fed from historical dams or reprocessed streams from primary chrome concentrators results in recoveries that ranges from 20 to 40%. This relatively high recovery is evident in the production performances at Northam's Eland re-treatment facility and Sibanye Stillwater's Rustenburg Western Limb Tailings Re-treatment (WLTR) and Platinum Mile operations (Northam RR 2020, 2021; Sibanye Stillwater RR 2016 – 2021; Anglo Platinum 2013 – 2017).

The plant tailings discharged from the Waterval concentrators fed to Platinum Mile were reported by Rule et al. (2008 to have 0.6 – 0.8 g/t 4E PGE content. While it has been more than a decade, the feed grade to Platinum Mile well correlates with Fig. 15, showing a relatively steady 4E PGM grade trend. Similarly, the 4E/6E PGM trend in tailings of overall operations in Fig. 12 of the major PGM producers in this review tends toward 0.4 – 0.6 g/t. It must be noted that the data in Fig. 12 is based on the overall reported company operations; individual operations of each company may have residual processed material 4E/6E PGM grades that may be as high as 0.8 – 1 g/t or greater or as low as 0.2 – 0.4 g/t. This is evident in Fig. 15 where the Rustenburg WLTR re-treatment plant records a grade pattern that is > 1 g/t, highlighting only operations at Rustenburg. Similar high average tailing 4E PGE grade at 0.88 g/t was reported at Marikana operations as well (Sibanye Stillwater AR 2019 – 2021). Platinum Mile scavenging flotation recovery yield was reported in the range of 4 – 10% during 2005 – 2007 (relative to the re-treatment plant feed grade) prior to its ultrafine grinding upgrade in 2009 (Rule et al., 2008). At an average ~ 0.65 g/t 4E feed grade, Platinum Mile recovery efficiency have improved over the decade ranging from 7 to 23% with an average recovery of 12% (Sibanye Stillwater AR 2009 – 2021). The Rustenburg WLTR re-treatment operation, now owned by Sibanye Stillwater, runs at a capacity of 4.6 – 4.8 Mtpa at a 4E PGE ~ 1 g/t grade achieving 30 – 40% recovery (Sibanye Stillwater RR 2016 – 2021). The Bulk Tailings Re-treatment (BTT) operation commissioned February 2018 by Lonmin Platinum (currently owned by Sibanye Stillwater) reported reprocessing of 2 Mtpa at 1.10 g/t achieving 21.3% recovery and producing 6E

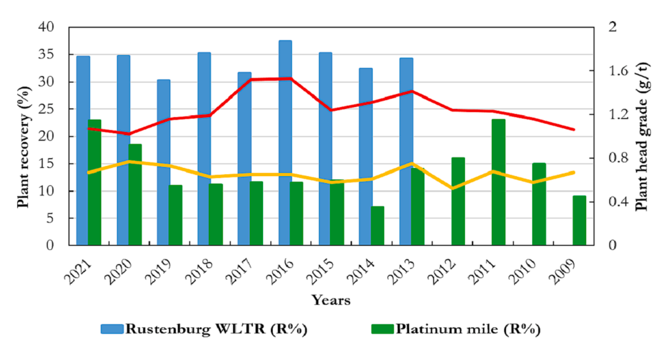

Fig. 15. Recovery and grade of reprocessed platinum group mineral tailings at Sibanye Stillwater's Rustenburg Western Limb Tailing Re-treatment and Platinum Mile re-treatment operations (Sibanye Stillwater RR 2016 – 2021; Anglo Platinum RR 2013 – 2017).

metals-in-concentrate representing 14,593 PGM ounces in 2018 (Lonmin AR, 2018). The scavenging plant has since re-treated about 3.6 Mt tailings annually at an average recovery of ~ 25% (Sibanye Stillwater RR 2019 – 2021). Eastern Platinum re-treatment PGM Zandfontein plant at Crocodile River Mine has been in operation since December 2020 reprocessing PGM tailings for residual PGM and chromite. The re-treatment operation has two plant facilities, Circuit B and Circuit D, running at current capacity of about 72 – 86.4 ktpm and 64.8 – 72 ktpm respectively (Eastplats 2022). The plant production performance from December 2020 to February 2022 reports an average plant feed grade and final tailing grade of 1.48 g/t and 1.35 g/t 6E, respectively, at an overall plant average recovery of 10.9 %. Recoveries are expected to increase, dependent on further optimisation and when steady state production is attained. Elsewhere, Ross et al. (2019), investigating the re-treatment of UG2 tailing using hydrodynamic cavitation, the authors reported that the rougher feed contained 0.69 g/t PGM at a 56% passing 75 μm and attained 63% recovery but at a trade-off lower concentrate grade (7 g/t 4E PGM).

Essentially, the information obtained from the literature and companies' published reports from both, tailings of primary concentration circuits and re-treatment circuits, demonstrate that PGM primary plant tailings and even re-treated tailings respectively hold considerable economic potential. Investigating what influences the high and low recovery trends in current industrial re-treatment circuits reviewed (as seen with Platinum Mile in Fig. 15) is beyond the scope of this paper. However, grade variability in the materials arising from historic legacy dams or primary chrome circuits and ongoing circuit optimisation at current operations are apparently the controlling factors for the recovery trends observed in different re-treatment operations. While current re-treatment recovery is low (10 – 12%), even this low recovery efficiency is still equivalent to an ~ 1% increase over the overall recovery of PGM primary concentrator. This represents significant profitability for the PGM concentration circuit (Rule et al., 2008). Of specific interest, as observed in the recovery efficiency of current industrial re-treatment circuits, is the fact that about 60% to even 90% of the re-treatment plant feed grade is retained in the overall final tailing deposition. This finding suggests that even the current re-treated tailings retain a high economic potential to be further valorised given feasible flowsheets and/or technologies exist to enhance the current recovery trend.

7. Summary and conclusion

The South African PGM industry produces large tonnages of flotation tailings annually. This massive stream is seen as a complex polymetallic secondary resource with an inherent very low value grade. Coupled with mineralogical challenges, the high yield achieved in well optimised primary treatment circuits results in tailings materials being less attractive for decades. However, the coming online of suitable technologies to meet challenges faced in the primary metallurgical treatment processes have led to growing interest tending toward tailings re-treatment to achieve profitability. Tertiary scavenging flotation characterises the recovery route for re-treating BIC flotation fresh online and dormant legacy tailings. Leading up to the tertiary flotation concentration stage, a number of pre-treatment configurations exist. Regrinding via tertiary ball milling and/or stirred milling, magnetic separation, gravity separation, and application of hydrodynamic cavitation devices are different unit stages that make up existing BIC re-treatment circuits in varying configurations. The pre-treatment selection depends on varying factors, importantly on the tailing parent mineralogy.

Value mineral deportment to the tailings stream is plant operation and ore type dependent. Tracing the value mineral to the final tailings, the long-aged problem of incomplete/partial liberation and fine-ultrafine flotation losses are prominent among the reasons for valuable mineral rejection. These primary causes have been addressed to some extent by the introduction of stirred mill, column flotation, and HCDs to improve primary plant and re-treatment circuits' grade-recovery relationship. The current industrial re-treatment processes economically achieve significant profit through smaller recovery increments (1 ~ 2%), known to have substantial impact on the overall primary process profitability. Nevertheless, about 60 – 90% of the re-treatment circuit head grade is still retained in the re-treated final tailings, which suggest that these materials have economic potential that can still be valorised further given feasible flowsheets and/or improved technologies to enhance the current re-treatment recovery efficiency. Although this review did not focus on mineral waste rocks, considering that even some of these materials contain residual PGM grains in the same order of magnitude as flotation tailings or maybe even more, these materials cannot be processed through milling circuits. Alternative routes for such materials require investigation. Such alternative processes, both for tailings re-valorisation and waste rock processing, could be achieved in non-concentrator routes, such as direct hydrometallurgical extraction, which may offer many opportunities, but have received very little attention to date. Essentially, the global drive toward net-zero emissions and the lack of substitutes for PGEs in their distinct applications highlight the need for valorising PGE flotation tailings streams, legacy dormant tailing, and mineral waste rock dump as an immediate approach to aiding the critical mineral supply from primary production processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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