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Hydrometallurgical extraction of platinum and palladium from oxidized PGE ores of the Bushveld Complex, South Africa – short report

»contract study«

Impressum

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Hydrometallurgical extraction of platinum and palladium from oxidized PGE ores of the Bushveld Complex, South Africa – short report

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Abstract

Jacobs University Bremen has been contracted by the Deutsche Rohstoffagentur (DERA) in Berlin to further develop a leaching technology for the mobilization of platinum group elements from oxidized ores of the Bushveld Complex, South Africa. The elements ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt) are clustered under the term PGE. The Great Dyke layered intrusion and the Bushveld complex in South Africa are the two largest PGE deposits worldwide. Current mining operations in both areas focus on the recovery of PGE from pristine ('fresh', unweathered) ores. Besides the pristine ore, the mineralogical composition of which is dominated by metal sulfides, there are huge surficial resources of oxidized Main Sulphide Zone (MSZ) and oxidized Platreef material. The pristine, sulfide-bearing ores are mined underground or from surface and are treated following conventional metallurgical practice (grinding, milling, flotation, smelting and production of a matte, chemical refining). The oxidized PGE ores are not mined because of insufficient recovery rates with conventional processing techniques. The challenges faced by the processing of these ores are largely caused by the complex and polymodal mineralogy of the PGE's and the hosting phases. In a past study, a leaching technology was developed to facilitate mobilization of Pt and Pd from oxidized PGE ores of the Great Dyke in Simbabwe and the Bushveld Complex in South Africa. In this study, the leaching technology named "2B-Platinum Leach" was optimized in terms of acid consumption and mobilization efficiencies and upscaling experiments at room and elevated temperatures were conducted in order to assess the economic viability of the process. The investigated oxidized heap ore samples had average Pt+Pd+Au (2E+Au) grades of 2.30 ppm. A maximum of 78% Pt, 55% Pd and 92% Au and on average 61% Pt, 46% Pd and 66% Au were mobilized in the course of the upscaling experiments at 80°C within 4 hours. Longer extraction times could lead to even higher recoveries. Therefore, the 2B-Platinum Leach technology is in principal economically viable, as demonstrated in a rough cost evaluation which is also part of this report.

Oxidized PGE ores constitute a great potential for satisfying the increasing PGE demand of Germany's and Europe's growing economies. Prospective automotive catalyst technologies and especially the regulations in the Euro 6 standard, which are mandatory in the EU for all automotive vehicles manufactured after 1. September 2015, will strongly increase the demand of the PGE. The chance of substitution of PGE is rather low due to their unique abilities as catalytic converters. Therefore, alternative PGE supplies such as oxidized ores need to be researched and economically exploited in order to meet the future demand and to minimize potential supply risks. Direct chemical leaching methods such as those developed within this research project have the potential to become future key technologies for bringing oxidized PGE ore deposits towards economic reality.

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	Introduction

1. Introduction

Jacobs University Bremen has been contracted by the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) in Hannover to conduct leaching experiments on oxidized platinum-group element (PGE) ore of the Platreef formation of the Bushveld complex in South Africa. The elements ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt) are clustered under the term PGE.

Oxidized PGE ores from the Bushveld Complex in South Africa and also from the Great Dyke in Zimbabwe have high potential for future mining because of relatively high PGE grades on the one hand and big resource estimates on the other (see Hey, 1999; Oberthür et al., 2012; Prendergast, 1988). In the Bushveld complex, resource estimates assume approximately 330 Mt of oxidized material, two thirds of which occur in the Platreef formation in the northern Bushveld complex. Within the oxidized PGE ores, the PGE are mainly hosted in Pt-Pd-oxides and -hydroxides as well as in Fe- and Mn-oxide and -hydroxide and clay-mineral-bound PGE. The mineralization is hosted in intensely weathered and serpentinized pyroxenites.

The deposits are surficial high tonnage low grade ore deposits ranging to maximum depths of about 15 to 30m, so that relatively low-cost open-pit mining of large volumes appears to be feasible. For the oxidized PGE ores in the Bushveld Complex, resource estimates are in the range of 337 Mt of oxidized material which contain about 819t or about 2.4 ppm of 4E (Pt, Pd, Rh, Au) (Buchholz & Foya, 2015).

The *pristine* material mined at those sites is treated following conventional metallurgical practice and recovery grades for Pt of more than 85% are reached (Rule, 1998). However, all metallurgical tests conducted so far on oxidized ore material suffer from very low Pt recoveries of considerably less than 30% (see Oberthür et al., 2012 and Kraemer et al. 2017). Relative to the pristine ore, the oxidized PGE ores, for example of the Great Dyke, which have a mineralogical and geochemical makeup similar to that of the ores of the Bushveld, show higher Pt/Pd ratios (due to depletion of Pd during weathering) and an almost

complete removal of sulphur (Locmelis et al., 2010). As reported by Locmelis et al. (2009), PGE in the oxidized Main Sulphide Zone (MSZ), which hosts most of the PGE resources at the Great Dyke, occur as relict primary platinum-group minerals (PGM; sperrylite, cooperite, braggite), in solid solution in relict sulphides as pentlandite, as secondary Pt-Fe alloys, as PGE oxides/hydroxides and as substitutes or adsorbed cations in iron-and manganese (hydr-) oxides. (Pt, Pd)-bismuthotellurides are almost completely destroyed (Oberthür et al., 2012). According to Oberthür and Melcher (2005), about 50% of Pt is hosted by PGM, 45% by hydroxide structures and 5% by relict sulfides. While the major element composition is mostly preserved in oxidized MSZ relative to its pristine counterpart, Oberthür & Melcher (2005) observed significant losses for Na, K, and S, which they assume to be caused by partial destruction of orthopyroxene, feldspar, phlogopite and sulphides - whereas Cu and Au were enriched during weathering due to immobile behaviour. The pronounced gain in LOI (loss on ignition) is according to Oberthür & Melcher (2005) caused by formation of hydrous silicates and formation of FeOOH in the oxidized ores. Apparently, the complex and strictly polymodal mineralogical state of the weathered PGE ores is the main cause of the processing issue faced with this ore deposit.

The processing of pristine PGE ores, the production of concentrates and the refining process of PGE (Fig. 1) are described in detail by Crundwell et al. (2011). The major steps in processing of PGE ores are flotation concentrate production (1), smelting and matte production (2), platinum concentrate production (3) and high-purity metal production (4). Crundwell et al. (2011) summarizes the processing of pristine PGE ores from mining to the refined metal.

The mined ore which contains roughly 3 to 10 ppm PGE is crushed and ground to liberate the sulfide mineral grains which host the PGE. The liberated mineral grains are separated by froth flotation with copper sulfate and xanthate or dithiophosphate (Crundwell et al. 2011). The flotation underflow is discarded and the froth is cleaned several times to produce a concentrate slurry with about 70 to 100 ppm PGE which is also highly enriched in Fe, Ni and other base metals like Cu and Co. This concentrate is dried and smelted to remove silica, iron and sulfur. This sulfur-deficient matte contains roughly 0.01-0.02% PGE, about 49% Ni, about 30% Cu and still 15-23% sulfur, which is needed for collection of the PGE by forming sulfide droplets in the melt. The matte is slowly-cooled and then either magnetically separated as is done in the Rustenberg refinery, South Africa, or, more commonly, leached over several (five or more) leaching stages to enhance the PGE concentrate and reduce or remove Ni, Cu and other (base) metal concentrations. At the final leaching stage, the concentrate contains about 50 to 70% PGE+Au. This concentrate is then completely dissolved in hydrochloric acid containing chlorine gas as an oxidant and the individual PGE's are selectively precipitated or separated from solution by a range of

processes such as precipitation with ammonium chloride or solvent extraction in case of Pt and precipitation with ammonium acetate, solvent extraction or ion exchange in the case of Pd.

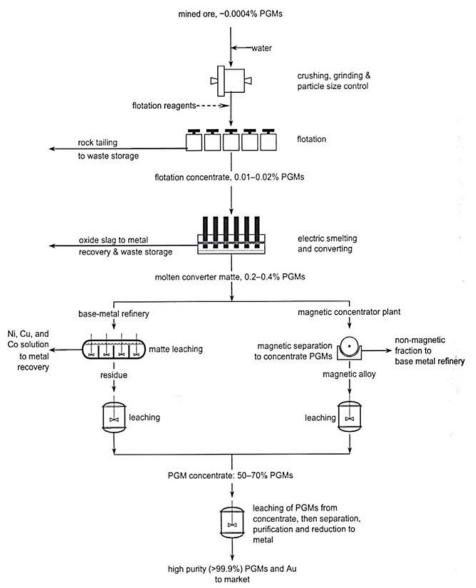


Fig. 1: Generalized flowsheet for the production of platinum group metals and gold from South African ore material (modified after Crundwell et al. 2011).

With conventional techniques, recoveries of Pt and Pd between 86 and 90 % are reached from pristine MSZ ores at the Hartley open pit mine in Zimbabwe (Rule, 1998).

One of the main issues faced with processing of near-surface oxidized PGE ores is the very heterogeneous PGE distribution over several mineral phases, including dispersion of PGE in secondary silicates and in iron- and manganese oxides/hydroxides. Another reason for the notably very low recoveries is concentrate dilution during froth flotation due to the occurrence of naturally floating gangue (NFG; Becker et al., 2009; Bulatovic, 2003) and lack of base metal sulphide association (Becker et al., 2014). Concentrate dilution during froth flotation is principally caused by the presence of talc-coated pyroxene grains, which

express a different flotation behavior in comparison to uncoated pyroxene grains. The polymodal distribution of PGE and occurrence of NFG are also the main issues faced with traditional processing of the oxidized ores described in this study. Already in 1939, Schneiderhöhn and Moritz noted that oxidized PGE ores cannot be processed by means of flotation, because the PGE minerals are too small and are covered by or coated with silicate minerals and/or weathering products - they suggested chemical leaching as the only remaining option for processing these ores. Prendergast (1988) reported processing trials of oxidized MSZ ores by means of gravity concentration and flotation and the reported recoveries were far below 50%. Oberthür et al. (2013) stated that metallurgical test work on oxidized MSZ ores from the Ngezi mine in Zimbabwe achieved Pt and Pd recoveries of only 15-30%. Kraemer et al. (2015) showed that Pt and Pd can be significantly mobilized from oxidized Great Dyke PGE ores using a leach technique which involves specific PGE-affine biomolecules. However, the technique faced relatively heterogeneous recovery rates depending on the origin of the actual sample and the exact weathering state of the ore, which are issues related to the polymodal distribution of PGE, both spatially and in relation to oxidation/weathering of the ore with depth. Significant portions of the near-surface oxidized ores present in the Mogalakwena Mine are already crushed, classified for 4E grades and stockpiled. Leach operations in the form of heap or tank leaches as indicated by Kraemer et al. (2015; 2017) and Mpinga et al. (2015) are probably the best-suited options for tackling the processing issue faced with near-surface oxidized ores.

In this study, the leaching technology 2B-Platinum leach was tested on heap material of oxidized Platreef PGE ores of the Bushveld District and an optimization in terms of reagent consumption and leaching efficiencies was conducted. Upscaling experiments with the optimized leaching technology were conducted in order to further assess economic viability of the process. Additionally, sequential leaching, or diagnostic leaching tests were carried out in order to assess the phase associations of base metals and of the precious metals Pt and Pd within the ores. The phase associations derived from sequential leaching can provide valuable information for tailoring and optimizing hydrometallurgical leaching techniques.

This final report covers information about the sample preparation, the experimental setups used for the sequential leaching as well as the optimization and upscaling of the 2B-Platinum leach and the chemical analysis conducted on the bulk rock samples as well as on the pregnant liquors. The report ends with an evaluation of the profitability of the process and a recommendation for future actions.

2. Samples

The samples used for the leaching experiments were collected by Jacobs University Bremen at Anglo American's Mogalakwena Mine in the northern Bushveld Complex close to the city of Mokopane (see Fig. 2).

At the Mogalakwena Mine, oxidized ores are removed as overburden in order to get access to the underlying pristine ores. These oxidized ores, however, are well characterized in terms of grades and kept separately from the barren rock material. The authors collected oxidized PGE ore material from six sites of a considerably large heap of about 6 Mt (Trust Muzondo, Anglo American, pers. comm.) at the Mogalakwena Mine. For sampling, the heap was subdivided into seven parts and representative surface samples were collected and homogenized on site. Approximately 30 kg of material was collected from each part, totalling approximately 180 kg of oxidized PGE ore. Jacobs University did not receive any 4E or XRF / XRD data from the cooperation partner Anglo American. The samples were shipped from South Africa to Jacobs University Bremen, Germany, immediately after collection for further processing.

upscaling experiments.
Sample ID
MOG_2016_101
MOG_2016_102
MOG_2016_103
MOG_2016_104
MOG_2016_105
MOG_2016_107

 Table 1: List of oxidized heap ore samples collected for the optimization and upscaling experiments.

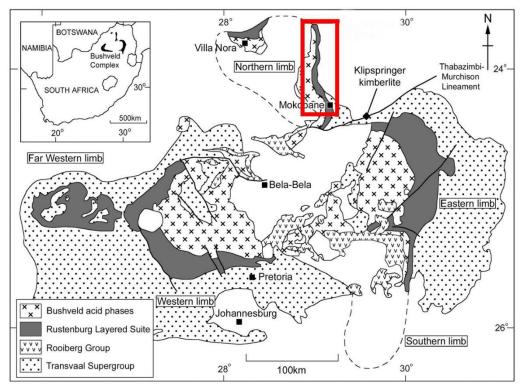


Fig. 2: Map showing the Bushveld Igneous Complex in the North-East of South Africa. Highlighted in red is the area of the sampling locality, the Mogalakwena Platinum Mine near Mokopane, Limpopo Province. Modified after Holwell et al., (2007).

3. Summary

Previous studies indicated that the oxidation/weathering of reef-type PGE ores from South Africa poses significant problems for the metallurgical extraction of the contained valuable metals (i.e., Becker et al., 2014; Kraemer et al., 2017; Prendergast, 1988, Oberthür et al., 2013 and others). The study presented here shows that the processing issue might be solved using the 2B-Platinum leach presented and optimized in the course of this study.

We showed that crushing of the oxidized heap ores is sufficient to enable high average recoveries in the subsequent leaching step. Comminution, and especially fine-milling of the ore material, adds significantly to the processing costs due to very high energy demands. In a big mining operation, the milling of the ores can easily exceed 50% of the total processing and mining costs. The heap ores investigated here only need to be crushed and not milled, which drastically decreases comminution and hence total mining costs.

On average, 52% Pt, 34% Pd and 29% Au were mobilized into solution during the upscaling experiments at 4 hours leaching times conducted within the course of this research contract. The recoveries achieved during the upscaling experiments, even at strongly elevated temperatures of 80°C, indicate that, in comparison to the small-scale lab

experiments, where Pt recoveries of nearly 70% were reached after 1 week leaching time at ambient temperatures, that the leach needs to be operated at much longer leaching times than those conducted for the upscaling experiments. However, despite rather intermediate recoveries, a big advantage of the proposed leaching process is the relatively low reagent cost. In the course of the optimization experiments, we could greatly reduce acid and other reagent consumption due to optimized reagent admixtures and optimized solid contents. The 2B-Platinum leach consists of inexpensive water, sodium chloride (rock salt, NaCl) and technical or industrial grade nitric acid. Market prices for the chemicals are in the range of 250 US-\$. It should be emphasized that these are consumer-prices and industrial-scale usage of these reagents would probably decrease reagent costs even further. Therefore, the cost scenarios below are calculated with 100% (scenario A), 60% (scenario B) and 30% (scenario C) of the prices indicated above. The reagent costs for scenario A can be calculated to be in the range of 68 US-\$ per tonne of ore, if no recycling of the reagents after extraction of the valuable metals is assumed. The reagent costs can be cut down to 40.8 US-\$ per tonne for scenario B and 20.4 US-\$ for scenario C. Platinum, Pd, Au and Ni are probably the main commodities that contribute the most to any revenue in the case of mining. The mean grades of the oxidized heap ores studied within this project are 1.18 ppm Pt, 0.92 ppm Pd, 0.197 ppm Au and 2050 ppm Ni. According to the market prices from March 2017, the total value of these four commodities alone are in the range of 93.8 US-\$ per tonne of oxidized ore. Nickel is excluded from the calculation at hand because of missing recovery data for the upscaling experiments due to analytical constraints as indicated above. Considering the average recoveries that were reached in the 40°C upscaling experiments (56% Pt, 34% Pd and 50% Au), a value of about 34.52 US-\$ per tonne of rock can be recovered in theory, whereas at 80°C (61% Pt, 46% Pd and 66% Au), 40.83 US-\$ per tonne of rock can theoretically be recovered. If 90% Ni recovery is assumed, the theoretically recoverable value per tonne of ore increases to 51.47 US-\$ for leaching at 40°C and 57.45 US-\$ at 80°C for four hours, respectively. Longer leaching times than those investigated here can probably increase recovery further as indicated above. Hence, with today's rather low metal market prices, the process is unprofitable for scenario A, but already profitable for scenarios B and C. Whether or not the small increase in recovered metal value between leaching at 40°C and 80°C justifies the additional energy needed to heat the leach liquor from 40°C to 80°C needs to be addressed in a detailed economic evaluation. If the reagent costs are subtracted for cost scenarios B and C, this leaves a margin of 12.54 US-\$/t for 40°C and 18.85 US-\$/t for 80 °C (scenario B) and 32.94 and 39.25 US-\$/t (scenario C). It should be noted that in most PGE mining operations, the platinum-group element Rh also contributes a significant portion towards the total revenue, but due to missing Rh data (Rh is not an established analyte at Jacobs Geochemistry Lab), Rh cannot be included in the calculation at hand. According to Anglo American, the heap of oxidized material already present at the Mogalakwena mine has a size of about 6 million tonnes. This material is in most parts crushed and probably needs no further comminution. The total 2E+Au content of the heap is about 444837 troy ounces. Therefore, about 306 Mio. US-\$ 2E+Au+Ni value can be recovered if the 2B-Platinum leach is operated at 40°C and 342 Mio. US-\$ if the leach is operated at 80°C. If the reagent costs are subtracted, this would leave a margin of at least 61.2 Mio US-\$ in the worst case (scenario B, 40°C) and could go up to 219 Mio. US-\$ (scenario C, 80°C).

Please note that this calculation is at most a "back-of-the-envelope" cost and revenue calculation and is only presented to show the general economic viability of the method. The calculation above does not include costs for positions like labor, energy, remediation, licenses and metal extraction, purification and marketing which must be subtracted from the margin calculated above for any revenue estimations.

Table 10: Evaluation of economic viability: Value per tonne of ore and value recovered if recoveries are assumed as achieved in the upscaling project.

	Average grades (ppm)	Market price 12.4.2017	Value per t of ore*	Value recovered with 2B-Platinum leach operated at 40°C per t of ore	Value recovered with 2B-Platinum leach operated at 80°C per t of ore		
Pt	1.25	31.04 US-\$ / g	38.8 US-\$	21.73 US-\$	23.67 US-\$		
Pd	0.99	25.58 US-\$ / g	25.32 US-\$	8.61 US-\$	11.65 US-\$		
Au	0.204	40.95 US-\$ / g	8.35 US-\$	4.18 US-\$	5.51 US-\$		
Ni	2210	10200 US-\$ / t	20.91 US-\$	18.82 US-\$ (assumed)	18.82 US-\$ (assumed)		
TOTAL			93.38 US-\$	53.34 US-\$	59.65 US-\$		

 Table 11: Reagent cost scenarios and calculated margin for labor, energy, refining and other costs per tonne of ore.

Cost scenario		Recovered value (40°C) - reagent costs	Recovered value (80°C) - reagent costs				
Scenario A (100% consumer price, no recycling)	68 US-\$ / t	-14.66 US-\$ / t	-8.35 US-\$ / t				
Scenario B (60% consumer price or 40% recycling rate)	40.8 US-\$ / t	12.54 US-\$ / t	18.85 US-\$ / t				
Scenario C (30% consumer price or 70% recycling rate)	20.4 US-\$ / t	32.94 US-\$ / t	39.25 US-\$ / t				

Table 12: Reagent cost scenarios and calculated margin for labor, energy, refining and marketing for the heap of oxidized material currently present at Mogalakwena mine (6 Mt ore) Cost scenario Recovered value Recovered value (80°C) - reagent (40°C) - reagent costs costs 408 -50.1 Mio. US-\$ Scenario A Mio. -87.96 Mio. US-\$ (100% consumer price, US-\$ no recycling) Scenario B 244.8 Mio. 75.24 Mio. US-\$ 113.1 Mio. US-\$ (60% consumer price US-\$ or 40% recycling rate) 19.764 Mio. US-\$ 122.4 Mio 235.5 Mio. US-\$ Scenario C (30% consumer price US-\$ or 70% recycling rate)

Table 13: Summary table showing ore grades and percentage mobilized in the upscaling experiments (mean of 20°C, 40°C and 80°C experiments at 4 hour experiment times) using the 2B-Platinum leach.								
	Ore grades				[%] recovered in upscaling experiments (mean of all 4h experiments)			
	Pt [ppb]	Pd [ppb]	Au [ppb]	Ni [ppm]	Pt	Pd	Au	
MOG_2016_101	1430	979	185	1840	44	28	33	
MOG_2016_102	1069	892	215	2125	34	40	20	
MOG_2016_103	1065	1050	179	2500	63	32	30	
MOG_2016_104	1545	1200	254	2290	51	30	31	
MOG_2016_107	1145	841	185	2295	68	41	32	
Average	1251	992	204	2210	52	34	29	

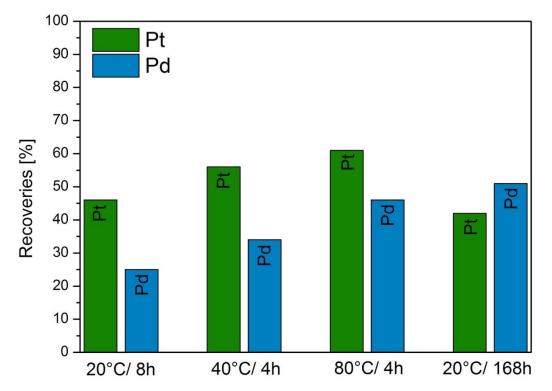


Fig. 15: Summary plot showing the mean Pt and Pd recoveries achieved during the short-term upscaling experiments at 20°C, 40°C and 80°C as well as during the one-week experiment at 20°C.

4. Recommendation

Our experiments demonstrated that Pt and Pd are efficiently extracted from oxidized ores using the 2B-Platinum Leach. The technology is, in principal, economically viable and further research needs to address whether it is possible (and economic) to selectively precipitate Pt, Pd, Au and the leached base metals from these leach liquors and whether or not these solutions can be regenerated for further use, which would even further decrease processing cost. If the process proves to be economically viable, further research hence has to focus on the extraction of Pt, Pd, Au and base metals from the pregnant leach liquors. Besides selective precipitation of the individual metals, promising frontier technologies are concentration and elution via tailor-made ion-exchange columns or the use of ionic liquids. Similar to the observations of Schneiderhöhn & Moritz (1939) and Oberthür et al. (2013), we conclude that chemical leaching is one of the key technologies for economically exploiting oxidized PGE ores, because many energy- and cost-intensive processing steps are evaded with direct chemical leaching of finely-ground ore. As stated by Crundwell et al. (2011), the traditional processing as applied for pristine reef-type ores in South Africa by the big producers consists of grinding, flotation, smelting of the ore, matte leaching with concentrated acids consisting of at least five individual leaching steps for base metal separation, adjacent multiple-step PGE leaching using concentrated acids and selective PGE precipitation. Many of the aforementioned steps require high energy and acid consumption, which leads, among others like increasing labor costs, to the fact that the cash costs per ounce PGM of most South African mining operations are still in the vicinity of the current metal prices (see e.g., Schmidt et al., 2015). This renders many current PGE mining operations (almost) unprofitable. The oxidized ores investigated here are surficial ores, i.e. easily extractable within the scope of open-pit mining operations and only need to be ground and hydrometallurgically treated in heap leach or reactor tank leach operations. According to Anglo American, the supplier of the oxidized heap ores investigated here, most of the oxidized ores occurring in the Mogalakwena open-pit mine are already excavated as overburden to gain access to the pristine ore below. These excavated and oxidized ores are already classified and deposited on heaps as (mineralized!) country rock. The heap that was investigated in this study has a size of about 6 million tonnes of ore material. Considering the average grades that were obtained in frame of this study, the resource of the heap of oxidized material accounts to 444837 troy ounces Pt+Pd+Au. Many open-pit PGE mines in the world have probably been excavating and stockpiling mineralized, but oxidized surface ores since the very first mining operation. However, to date, many of these oxidized ores are not mined due to very low recoveries with all known (hydro)metallurgical technologies. The reserves and grades of oxidized PGE ores at the Great Dyke in Zimbabwe, for example, are

almost as high as those of the Bushveld (Oberthür et al., 2013). In addition to the Main Sulphide Zone of the Great Dyke and the Platreef of the Bushveld intrusion, there are additional reports on the occurrence of significant portions of oxidized PGE ores within, for example, the Merensky Reef (Korges, 2014) or the UG-2 chromitite in the Bushveld, the Stillwater Complex in Montana (Fuchs & Rose, 1974) and the Lac de Iles deposit in Canada (Hattori & Cameron, 2004). Therefore, oxidized ores definitely represent an important supplier for the mining of these critical high-technology metals in the near future. Oxidized PGE ores constitute a great potential for satisfying the growing PGE demand of Germany's and Europe's economies. Prospective automotive catalyst technologies and especially the regularized Euro 6 standard which is mandatory for all cars in the EU manufactured after 1. September 2015, will probably significantly increase the demand for PGE. The chance for substitution of PGE is rather low due to their unique abilities as catalytic converters. Therefore, alternative PGE suppliers like oxidized ores need to be researched in more depth and economically exploited in sustainable manners in order to meet the future demand of the world economy and to minimize potential prospective supply risks.

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