



Improving recoveries of platinum and palladium from oxidized Platinum-Group Element ores of the Great Dyke, Zimbabwe, using the biogenic siderophore Desferrioxamine B



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ABSTRACT

This study presents results of batch leaching experiments conducted on oxidized (weathered) Platinum-Group Element (PGE) ores from two platinum mines at the Great Dyke, Zimbabwe. The Great Dyke mafic/ultramafic layered intrusion is, after the Bushveld complex in South Africa, the second largest PGE deposit worldwide. Current mining operations focus on the recovery of PGE from pristine and unweathered ore material from the Main Sulfide Zone (MSZ). Besides pristine ores, there are significant resources of oxidized MSZ material at or near the surface. These oxidized PGE ores are currently not mined because insufficient recoveries using conventional processing techniques render this process option uneconomical. The complex, polymodal mineralogical distribution of the PGE in the oxidized MSZ aggravate to the processing issue. The data presented in this study show that a mild hydrochloric acid leach combined with a subsequent leach with the biogenic siderophore Desferrioxamine B (DFOB) in an aqueous solution efficiently extract Pt and Pd from these ores. Although Pt and Pd extraction during hydrochloric acid pretreatment is rather heterogeneous with a maximum Pt recovery of 30%, it nevertheless facilitates mobilization of Pt and Pd in the subsequent siderophore leaching step. Hydrochloric acid pretreatment of the oxidized PGE ores is a prerequisite for liberating the PGE-bearing host phases from weathering products and for the reduction of the amount of easily-available cations such as Fe in hydroxide minerals, which may compete with Pt and Pd for complexation in the subsequent siderophore leach step. This two-step approach results in a combined extraction of up to 80% of total Pt. Our results further show that Pt and Pd extraction during siderophore leaching is strongly pH-dependent and appears to be most efficient at near-neutral to slightly alkaline conditions, with increasing extraction efficiencies at higher pH. Based on the results of this study, siderophore leaching of oxidized (PGE) ores represents a promising approach for the hydrometallurgical extraction of Pt and Pd from oxidized ores.

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1. Introduction

The metals ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt) comprise the Platinum-Group Elements (PGEs). Oxidized PGE ores from the Great Dyke in Zimbabwe have high economic potential for future mining because of the combination of relatively high PGE grades and large resource estimates (Prendergast, 1988; Oberthür et al., 2013). They are surficial ore deposits ranging down to maximum depths of about 15 to 30 m, allowing relatively low-cost open-pit mining of high volumes. For the oxidized PGE ores of the Great Dyke, resource estimates range from 160 to 250 Mt of oxidized material (Oberthür et al., 2013) with average grades of 3–5 ppm Pt, i.e. 480–1250 tons of Pt metal are contained in these deposits.

The pristine (i.e. unweathered or “fresh”) sulfide-bearing PGE ores mined at the Great Dyke are processed following conventional metallurgical practice. This includes froth flotation of milled material, smelting and matte production, and chemical leaching (Crundwell et al., 2011). The metallurgical processing route for pristine material reaches Pt recoveries of >85% (Rule, 1998).

The processing of weathered, oxidized PGE ores, however, is challenging, because PGE extraction with conventional techniques is too inefficient to be economically feasible. Metallurgical tests conducted on oxidized ore material from the Great Dyke suffer from very low Pt recoveries of considerably less than 30% (Oberthür et al., 2013).

The complex polymodal distribution of the PGE is a major challenge for upgrading and processing of this supergene ore and prevents commercial mining (Oberthür et al., 2013). Becker et al. (2014) attributed the poor flotation performance of oxidized PGE ores to a combination of poor PGE mineral liberation, a lack of base metal sulfide association and especially the presence of naturally floating gangue (NFG; Becker

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et al., 2009; Bulatovic, 2003). The oxidized PGE ores from the Great Dyke, Zimbabwe, contain high amounts of NFG (mostly talc and talc-coated orthopyroxene grains; e.g., Becker et al., 2013). The presence of these phases leads to an effective dilution of the concentration grades during flotation. This in combination with the aforementioned factors ultimately results in a considerably decreased flotation performance whenever oxidized portions are present during flotation of PGE ores (Becker et al., 2014).

To address the processing issue, we conducted batch leaching experiments using specific low-molecular weight organic molecules known as siderophores, to extract Pt and Pd directly from oxidized PGE ores.

Siderophores are a group of organic molecules synthesized and exuded by plants and bacteria in oxic environments to mobilize and bind trivalent Fe from oxyhydroxide mineral structures. However, besides having high affinities for Fe, most siderophores are also very effective in binding and solubilizing many other elements such as the rare earth elements and yttrium, some PGE and some actinides (Bau et al., 2013; Christenson and Schijf, 2011; Desouky et al., in press; Liermann et al., 2011; Duckworth et al., 2009; Bellenger et al., 2008; Dahlheimer et al., 2007; Mullen et al., 2007; Yoshida et al., 2004, 2007; Brantley et al., 2001; Baysse and Vos, 2000; Bouby et al., 1998; Hernlem et al., 1996, 1999). Kraemer (2004) compiled a detailed review of siderophore chemistry and interactions with metals.

The siderophore used in the present study is the trihydroxamate siderophore Desferrioxamine B (DFOB), a common siderophore produced by the actinobacteria *Streptomyces pilosus* and others (Müller et al., 1984). The molecule occurs in many soils (Winkelmann, 1992) and natural waters (Gledhill et al., 2004; McCormack et al., 2003) at concentrations in the nano- to millimolar range.

Solution speciation and metal binding modes of DFOB are discussed by Kiss and Farkas (1998), for example. DFOB contains three hydroxamate functional groups and a terminal amine. The terminal amine does not deprotonate except at very high pH and thus usually does not take part in the complexation reaction (see deprotonation of DFOB in Table 1; e.g. Christenson and Schijf, 2011; Hernlem et al., 1996). In the case of Fe complexation, each of the three hydroxamate functional groups forms a five-membered ring with the trivalent Fe thus satisfying the preferred octahedral inner coordination sphere of Fe (Kraemer, 2004).

The dissolution of metal oxides by siderophores is mostly a ligand-promoted dissolution mechanism with a one on one stoichiometry (Kiss and Farkas, 1998), although reductive and oxidative mechanisms as a result of electron transfer between surface metal and absorbed ligands have also been suggested (see Bau et al., 2013; Bi, 2009; Yoshida et al., 2004 and others). A study by Mohwinkel et al. (2014) demonstrated that DFOB may be a viable reagent in the extraction of high-technology metals like Mo from deep-sea ferromanganese nodules and crusts.

Dahlheimer et al. (2007) conducted experiments on the siderophore-mediated mobility of PGEs in soils and provide metal stability constants for DFOB complexes: Except for tin, Pd and Pt have the highest metal stability constants (Pd: $\log K_f = 19.2\text{--}23.2$; Pt: $\log K_f = 16.2\text{--}17.2$) of all divalent metals investigated for hexadentate DFOB complexation. Hence, the extraction of PGE from oxidized PGE ore material with siderophores might be a promising approach, sole or in combination with other acids, for improving the recoveries of PGE from oxidized ores.

The combination of mild hydrochloric acid leach steps with siderophore-mediated extraction of Pt and Pd as presented in this study may be a first step towards the development of a successful process route for material from this special type of currently unexploited ore deposit.

2. Experimental

2.1. Samples

The ore samples used in the experiments originate from the Ngezi Mine and the Hartley Open Pit Mine of the Great Dyke in Zimbabwe and were gratefully provided by Zimplats Inc.

In the Great Dyke, according to Oberthür and Melcher (2005), economic concentrations of PGE, Ni and Cu occur in the form of disseminations of mainly intercumulus sulfides in the Main Sulfide Zone (MSZ). The MSZ is generally between 1.5 and 4 m wide and outcrops to the rims of the Great Dyke on the western and eastern limbs. The MSZ shows the highest PGE grades (3–5 ppm) and thus is the major PGE resource of the Great Dyke.

Close to and at the surface, the MSZ is intensely weathered and oxidized to depths of about 15 to 30 m. Relative to the pristine ore, the oxidized PGE ore shows higher Pt/Pd ratios indicating depletion of Pd during weathering and almost complete removal of sulfur (Locmelis et al., 2010). As reported by Locmelis et al. (2010), PGEs in the oxidized MSZ usually occur as relict primary Platinum Group Minerals (PGM; sperrylite, cooperite, braggite), in solid solution in relict sulfides like pentlandite, as secondary Pt–Fe alloys, as PGE oxides/hydroxides and as substitutes or adsorbed cations in Fe and Mn (hydr)oxides. (Pt, Pd)-bismuthotellurides and sulfides (pyrrhotite, pentlandite, chalcopyrite and subordinate pyrite) are almost completely destroyed (Oberthür et al., 2013). According to Oberthür and Melcher (2005), in oxidized MSZ about 50% of the Pt is hosted by discrete PGE oxide and hydroxide minerals, 45% is hosted in either Mn- or Fe-hydroxide structures, and 5% by relict sulfides.

The batch leaching experiments presented here were conducted on two types of sample material. The PtOx composite sample is a mixed sample which contains so-called peak material (i.e. parts of a drill core showing highest Pt grades in the profile) of four different drill cores of the Ngezi Mine. The other two samples, PtOxN001 from the Ngezi Open Pit Mine and PtOxHOP001 from Hartley Open Pit, are made up of Pt peak material of a single drill core.

In both ‘peak’ samples, PtOxHOP001 and PtOxN001, subhedral to euhedral cumulus orthopyroxene grains (>80 vol.%) are the most abundant minerals with grain sizes ranging from 1 to 3 mm. Olivine (5 vol.%), interstitial clinopyroxene and interstitial plagioclase are present. Further, some relict sulfide grains are observed in particular in PtOxN001. Relict PGM were observed by electron microprobe (Fig. 1a). In PtOxHOP001, clay minerals, such as smectite and willemseite, occur as secondary minerals whereas in PtOxN001 only minor amounts of these clay minerals are present. In PtOxHOP001, (Pt, Pd)-oxides were identified using electron microprobe as shown in Fig. 1b. Secondary minerals like oxyhydroxide minerals (viz FeOOH and Mn–Ni–Co–OOH), which formed during weathering, are significantly enriched in Pt and Pd with 50–80 ppm Pd and up to 400 ppm Pt (see Fig. 1c, d).

The dried and crushed samples were powdered with a Fritsch Pulverisette-6 planetary mill with agate balls and a sealed agate mortar.

The elemental composition including Pt and Pd grades for all samples are presented in Table 2.

2.2. Leaching

All lab work related to this project was conducted in a trace-metal clean environment. The siderophore mesylate salt of DFOB, Desferal®, is sold as a drug to treat iron hemochromatosis and was used in this

Table 1

Reactions and formation constants for the protonation of the siderophore Desferrioxamine B (DFOB) as obtained from Martell and Smith (2001).

Reaction	$\log K_{298}$; $I = 0.1$
$DFOB^{3-} + H^+ \leftrightarrow H_1DFOB^{2-}$	10.84
$DFOB^{3-} + 2H^+ \leftrightarrow H_2DFOB^{-}$	20.39
$DFOB^{3-} + 3H^+ \leftrightarrow H_3DFOB$	29.37
$DFOB^{3-} + 4H^+ \leftrightarrow H_4DFOB^+$	37.69

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