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Towards cleaner production – Using flotation to recover monazite from a heavy mineral sands zircon waste stream

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ABSTRACT

In line with the principles of cleaner production, the removal of monazite via reverse flotation was investigated with a view to reducing the radioactivity of a heavy mineral sands waste stream. Another benefit was to create a potential REE by-product from the Namakwa Sands operation in South Africa. Understanding the mineralogy of the zircon waste stream was essential owing to the cemented nature of the deposit and the potential impact of surface coatings on the flotation performance. SEM, QEMSCAN and optical microscopy showed that amorphous SiO_2 was the most abundant surface coating associated with both monazite and zircon, which is likely to constitute a major challenge in achieving flotation selectivity. A D-optimal statistical screening design was applied to find the most relevant flotation parameters and a full factorial design to find the optimal flotation conditions. The most promising results showed that monazite could be successfully removed from the zircon waste with an oleate collector at pH 10. The selectivity was found to be highly dependent on pH, with no selectivity at pH 9 and no mineral flotation at pH 11. Further work is recommended to confirm and optimise these conditions and test them on a larger scale.

1. Introduction

The mining industry is continually challenged to achieve more sustainable production with less negative environmental impact. The traditional and most commonly used method of tailings disposal is to store waste produced by mineral processing in large unsightly dams. Some of the challenges linked to maintaining tailing dams include the handling and storage of these large volumes, as well as the slow settling of fine particles that can hinder the recycling of water (Edraki et al., 2014; Wang et al., 2014). Hazardous processing chemical residues and acid conditions caused by oxidising sulphide minerals further complicate water recycling and are a risk for the environment if released without treatment. Alternatives to conventional tailing storage facilities are paste and thickened tailings that can be deposited on the surface or as backfill underground. It is also possible to implement the reuse, recycling and reprocessing of tailings. The review paper by Edraki et al. (2014) provides examples of several attempts to reprocess tailings, such as using waste in brick making, separating valuable minerals with gravity concentration, removing gangue minerals by means of flotation and using leaching or bioleaching of tailing deposits to extract metals. Reducing mineral processing waste would improve sustainability in the mining industry; thus, a greater focus on sustainable development in respect to the reuse of mining and mineral processing waste should be considered (Bian et al., 2012). Waste reprocessing is in line with cleaner production, which is an initiative to increase product efficiency and minimise waste and pollution (not to be confused with the conventional use of 'cleaner circuits' in the context of flotation). Cleaner production is used in many industries including the mining industry (Hilson, 2000, 2003; Silvestre and Silva Neto, 2014) and is part of the United Nations Environment Programme.

In the processing of heavy mineral sands, handling and disposal of radionuclides is a concern (World Nuclear Association, 2015). In particular, the thorium and uranium containing mineral monazite is one of the main contributors to radioactivity and can be hazardous when concentrated in the products and wastes of heavy mineral sands processing. Monazite ([Ce,La,Nd,Th]PO_4), however, is also well known to be one of the main host minerals of the light rare earth elements (LREE), for which there is currently a significant demand for use in cell phones, laptops, catalysts for fuel production and green technology in wind power turbines (Hurst,

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2010; Jordens et al., 2013). Therefore, opportunity exists to recover the valuable rare earth elements (REE) as a by-product, while simultaneously reducing the environmental risk of the tailings.

Valuable heavy minerals such as zircon ($ZrSiO_4$), rutile (TiO_2) and ilmenite ($FeTiO_3$) are generally separated from the gangue minerals in heavy mineral sands deposits using a combination of physical separation techniques. Ilmenite is separated based on its magnetic properties, and thereafter zircon, rutile and monazite are separated based on their conducting and magnetic properties (Jones, n.d). Zircon and monazite are both non-conductors and must be separated using their magnetic properties. One of the challenges in a heavy mineral separation plant is to produce a clean zircon concentrate without the monazite that has reported to the cleaning circuit. This frequently means sacrificing zircon recovery by producing a waste stream with monazite and high zircon grade. This is particularly so in the fine sizes: wet gravity and electrostatic separation methods are efficient for coarse particle sizes, but generally fail to recover particles <100 μm (Wills and Napier-Munn, 2006). Consequently, waste streams from cleaner electrostatic separation circuits may have a fine size fraction containing valuable minerals such as zircon, rutile and monazite. One of the few mineral separation techniques that have an operating window which is ideal for particles in this size range is flotation.

The successful separation of monazite from zircon using flotation has been reported by several authors (Bruckard et al., 1999; Cheng et al., 1993; Cuthbertson, 1951; Jordens et al., 2015; Pavez and Peres, 1993; Ren et al., 2000). Cuthbertson (1951) secured a patent for monazite flotation from heavy minerals such as wolframite, rutile and cassiterite using boiled starch as the depressant and an amine collector. Thereafter, Abeidu (1972) studied the separation of monazite from zircon using experiments in a Hallimond tube with an oleic acid collector and Na_2S as a monazite activator. Pavez and Peres (1993) more specifically studied the monazite-zircon-rutile flotation system. Sodium oleate and hydroxamate collectors were used, with metasilicate to depress zircon and rutile. Both collectors showed promising results in the Hallimond tube experiments. The best reagent regimes were subsequently repeated using bench scale flotation by Pavez and Peres (1994) resulting in both high monazite recovery and good depression of rutile and zircon. The flotation of monazite from a zircon flotation tail was performed by Bruckard et al. (1999), and reverse flotation of a titanium-rich product was studied by Bruckard et al. (2001) by floating monazite and zircon. However, few attempts to separate monazite from zircon were made in either of the studies by Bruckard et al. A recent paper by Kumari et al. (2015) noted the lack of any common view of a standard reagent regime for monazite flotation and highlighted the need for a better understanding of the physio-chemical properties of monazite.

Apart from understanding the physio-chemical properties of monazite, the ability to investigate selected factors influencing the flotation system is also needed. Of interest in this study is the role of process mineralogy and statistical design. The understanding of mineralogy is important to gain knowledge about the valuable and deleterious element deportment, bulk mineralogy, mineral liberation and association, grain size distribution and characteristics of any well-developed coatings on the mineral surfaces. Long standing techniques such as optical microscopy (Jones, 1987), as well as the more modern techniques which are based on the Scanning Electron Microscope (SEM) coupled with energy dispersive X-ray spectroscopy, provide a useful platform to investigate these features in ores and processing streams (Fandrich et al., 2007; Lamberg and Rosenkranz, 2014; Restarick and Gottlieb, 1991).

Similarly, the design of experiment (DoE) approach is essential to control and evaluate the factors that influence flotation performance. The use of DoE allows for objective conclusions to be drawn due to the statistical methods that are used in the experimental methodology (Antony, 2003). The full factorial design is an experimental method where tests with every possible combination of the chosen factors and levels are carried out. The advantages of factorial design are many (Napier-Munn, 2014): it allows for the determination of the linear interactions between variables, it estimates the main effects efficiently as every test includes information about all factors, and it provides a good estimation of error.

The objective of this paper is to investigate the mineralogy and the potential to separate monazite from a terminal zircon waste stream by flotation with a case study from the Namakwa Sands heavy mineral deposit in South Africa. The attempt to produce a monazite product enriched in La, Ce, Nd and radioactive components, and a zircon product that potentially meets the specifications of an additional low grade zircon product (<0.5% TiO_2, 1000 ppm U and Th) brings the heavy mineral sands industry one step closer to achieving cleaner production.

2. Material and methods

2.1. Namakwa Sands

The Namakwa Sands operation, owned by Tronox Limited, currently upgrades the heavy mineral sands deposit to produce rutile (TiO_2), ilmenite ($FeTiO_3$) and zircon ($ZrSiO_4$) concentrates that are processed and separated based on density, magnetic and conducting properties using wet tables and spirals, and magnetic and electrostatic separation. The annual production capacity is 21 Mt run-of-mine ore (Philander and Rozendaal, 2013).

The deposit consists of 8 wt.% heavy minerals (Philander and Rozendaal, 2013) comprising ilmenite, rutile, zircon, leucoxene, garnet and pyroxene as the dominant heavy minerals. The deposit is divided into two major ore bodies, the Graauwduinen West and Graauwduinen East deposits. The East deposit is a typical, loosely consolidated minerals sands deposit, whereas the atypical West deposit consists of heavy minerals in a cemented matrix (known as 'cemented hard layers'; Philander and Rozendaal, 2013). Consequently, ore from the West deposit needs comminution to liberate the valuable minerals, as well as attritioning and hot acid leaching to remove surface coatings in order to achieve better separation. The most common surface coatings in the operation are clay colloidal coatings: sepiolite, sepiolite with calcite, calcite, apatite and opaline silica. These surface coatings, which affect mineral surface properties, are likely to have an impact on flotation performance.

Monazite is one of the gangue minerals and varies between 0.08% and 0.36% of the total heavy mineral content of the deposits. Its composition is presented in Table 1. The monazite at Namakwa Sands is enriched in the LREE, lanthanum, cerium and neodymium. The mineral chemistry also indicates that monazite is a significant

Table 1
Average major oxide chemistry (wt.%) of monazite in the Namakwa Sands deposit (Philander and Rozendaal, 2009).

	Monazite
SiO_2	8.72
CaO	2.66
P_2O_5	32.03
La_2O_3	15.15
Ce_2O_3	32.20
Nd_2O_3	9.10
ThO_2	2.07