Zircon surface characterization

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Synopsis

Surface coatings persisting on zircon particles, after being leached in an acidic solution, are believed to be the cause of zircon misplacement during the electrostatic separation of heavy mineral beach sands. Electrostatic separation is employed to separate non-conductive zircon particles from more conductive rutile particles. Surface coatings on zircon particles are believed to render the non-conductive zircon particles more conductive, resulting in the contamination of the more conductive rutile stream with zircon particles. Resistivity measurements, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were performed to compare the surface characteristics of zircon particles found in the different product streams following electrostatic separation. XPS analysis showed that no significant difference exists in the outermost layer of the zircon particles found in the different streams. SEM analysis showed the existing surface coatings on zircon particles from different product streams to have similar chemical compositions. Resistivity measurements confirmed the results obtained from both the XPS and SEM analysis; no significant differences in the resitivities were observed. From the results obtained it suggests that surface coatings present on zircon particles are unlikely the primary cause of zircon misplacement. Zircon losses can possibly be a result of machine related aspects.

Key words: XPS; SEM; resistivity measurements; electrostatic separation; heavy mineral sands.

Introduction

Exxaro KZN Sands' heavy mineral treatment plant is situated near Empangeni in KwaZulu-Natal, South Africa, and produces magnetic ilmenite and non-magnetic zircon and rutile. Electrostatic separation is used to separate the non-conductive zircon fraction from the more conductive rutile fraction, based on the conductive properties of the different mineral particles[1,2]. Industrial investigations of non-magnetic treatment section (electrostatic separation section) indicate the misplacement of non-magnetic zircon particles incorrectly to the more conductive rutile stream.

Although various physical parameters, such as temperature and humidity, can influence particle resistivity[3], it is believed that surface coatings present on the zircon particles result in the misplacement. Leaching at elevated temperatures under acidic conditions is utilized to remove excessive surface coatings; however, it is believed that the remaining coatings and stains result in zircon particles behaving less resistively[4].

According to Gerson *et al.*[5] surface coatings occurring on zircon particles consist mostly of mixtures of hydrated iron oxides and hydroxides (limonite), clays and colloidal silica. These foreign materials are believed to cause the non-conductive zircon particles to behave more conductively, resulting in zircon particles reporting incorrectly to the more conductive rutile stream.

The aim of this project was to characterize the surface properties (by employing resistivity measurements, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM)) of zircon particles found in the conductor and non-conductor fractions and to determine if these properties are possibly related to the misplaced zircon particles during the electrostatic separation of zircon and rutile.

Experimental

Sampling and sample preparation

Industrial samples were obtained from the conductive and non-conductive streams of the final electrostatic separation step in the non-magnetic treatment section of the Empangeni plant. Repetitive electrostatic separation and hand-picking were used to separate the zircon particles from both these streams for further test work.

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Particle size distribution (PSD) analysis was performed on the two streams prior to the separation of the zircon particles. It was found that less than 1% of the particles from both streams reported to the size fraction smaller than 63 micron, which ruled out the possibility of zircon misplacement due to particle entrainment onto the separation rotor[6].

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS)[7] was utilized to obtain the composition of the outermost layers (~3 atom layers) of the zircon particles from the two streams; compositional variations in the outermost layer may result in differences in the surface resistivities. Hand-picking of the zircon particles (to a total mass of ~ 1 gramme) from the various streams was required for adequate accuracy. A Physical Electronics model 5400 quipped with an Al/Mg dual X-ray source and an Al monochromator was used for the XPS analysis.

Scanning electron microscopy (SEM)

SEM analysis was used to determine the composition of the macroscopic surface coatings existing on the zircon particles found in the different streams. A Jeol JSM 6300 with a Noran EDS system operated at various accelerating voltages was used for the SEM analysis.

Resistivity measurements

Resistivity measurements were performed to resemble the physical conditions existing at the industrial processing plant. The method described by Venter *et al.*[8] was used to obtain resistivity measurements of zircon particles at an 80% relative humidity (at 35°C) and at a separator feed temperature of 80°C. The total moisture content of the samples was measured after each experimental run, ranging in a narrow band between 0.02 and 0.04% (by mass). The zircon particles were packed into a resistivity cell to form a packed bed, across which resistivity measurements were taken. Current measurements were obtained using a Keithley (model 614) electrometer. A Keithley 428 current amplifier was installed to amplify the obtained currents, while a constant voltage of 95.6 V (direct current) was maintained across the cell. The zircon particles used for these measurements were separated from the non-conductive zircon stream and the more conductive rutile stream by means of repetitive electrostatic separation stages.

These resistivity measurements were complementary to the XPS and SEM analysis; differences in the surface and macro characteristics are expected to result in differences in the resistivity measurements.

Results and discussion

Figure 1 shows a survey of the surface composition found on the zircon particles from the different streams using XPS analysis. Note that the conductive plot was obtained from the zircon particles obtained from the more conductive rutile stream, while the non-conductive plot was obtained from the zircon particles obtained from the non-conductive zircon stream. The spectra analysis shows the five elemental species occurring in the outermost layer.

From the plot it appears that no significant differences exist between the compositions of the different fractions' outermost layers. No foreign species seems present on either of the fractions and in addition the species appear to be present in the same amounts. The elements identified, the transition state and binding energies are summarized in Table I. The observed indium is used as a mounting agent for the zircon particles.

In addition to the spectral analysis (50–1 000 eV), an examination of each of the individual elemental peaks was performed to determine if a difference in phase occurrence or oxidation states was present. This was established by drawing up a multiplex and analysing the obtained peaks to see if any differences in the various peak forms occurred. All these comparative studies showed no significant differences in the surface species.

Figure 2 shows the back-scattered electron images of the surface coatings, which were analysed using energy dispersive X-ray (EDX) analysis. Random analysis of coatings in the different streams, using SEM analysis, showed no significant difference between the cation compositions of the coatings,; indicating that the chemical composition of these oxides is probably not the cause of the

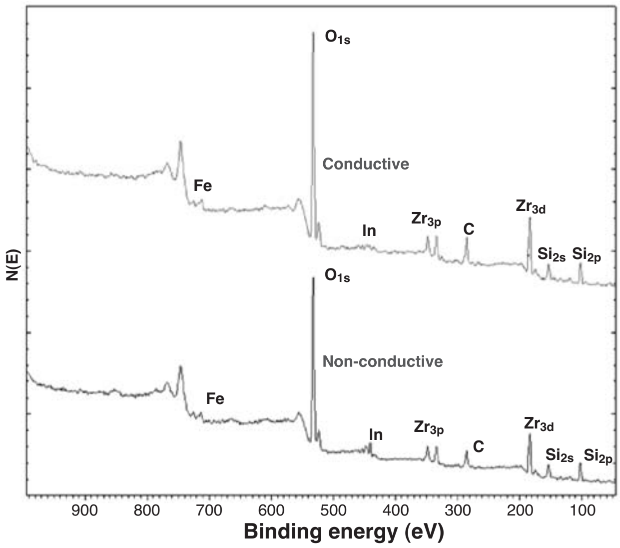

Figure 1—XPS surveys obtained during the XPS analysis of the zircon particles from the different streams

Table I

XPS analysis of the species present on the zircon surface

Element	Transition	Binding energy (eV)
Fe	$2p_{3/2}$, $2p_{1/2}$	715–730
O	1s	530–540
Zr	$3p_{3/2}$, $3p_{1/2}$	335–355
C	1s	285–290
Zr	$3d_{5/2}$, $3d_{3/2}$	170–195
Si	2s	155–165
Si	2p	95–110

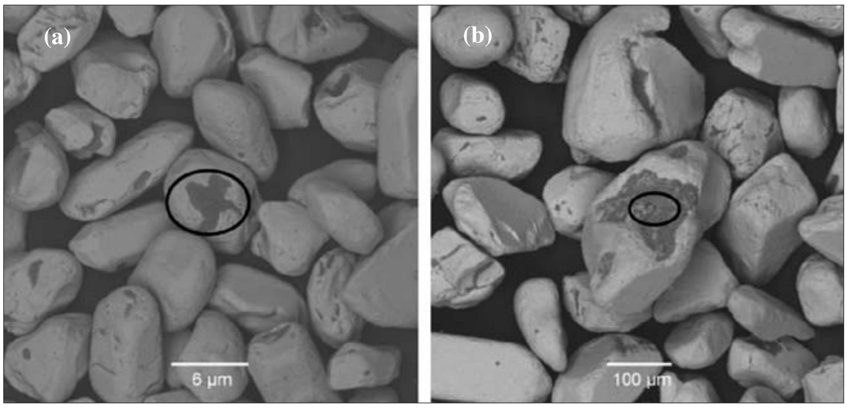

Figure 2—Back-scattered electron images showing typical coatings (circled in black) existing on the more conductive (a) and non-conductive (b) zircon particles (Magnification: Figure 2(a) x180 at 15 kV acceleration voltage; Figure 2(b) x150 at 15 kV acceleration voltage)

Table II

Average resistivities of the conducting and non-conducting zircon fractions

	Average (Ω.m)	Standard deviation
Conductor	2.87×10^{10}	1.58×10^{10}
Non-conductor	2.83×10^{10}	1.49×10^{10}

zircon misplacement. The majority of the coatings consisted of Al, Si and O, occurring predominantly as aluminium silicates.

Table II summarizes the resistivity measurements conducted on the zircon from conductor and non-conductor fractions; the resistivity values correlate with data published by Holtham *et al.* [3]. The resistivity measurements showed no significant difference between the resistivities of the zircon particles in the conductor and non-conductor streams.

The resistivity measurements clearly support especially the XPS investigations; no significant differences in the surface composition as indicated by the XPS analysis reflected similar conductivities for the streams under investigation. This strong evidence indicate that the misplacement of zircon to the conductor fraction is probably not strongly related to differences in the surface composition; coatings are unlikely the cause of this misplacement. Preliminary electrostatic investigations performed on the same industrial sample suggest machine settings (for instance, feed rate) to be a possible cause for the losses.

Conclusion

XPS analysis showed no significant differences in the composition of the outermost layers of the zircon particles from the different electrostatic separation streams. SEM analysis showed similar compositions for the surface coatings existing on the zircon particles from the different electrostatic separation streams; surface stains occurring after leaching are unlikely to have a detrimental effect on the particle conductivities. Resistivity measurements performed on the zircon particles confirm XPS results; the misplacement is probably not a result of differences in the surface chemical composition and coatings are therefore unlikely to be the cause of misplacement.

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