1. INTRODUCTION

Zirconium and its compounds have in recent years received increasing attention, due to new fields of application. Zirconium chemicals are used in, amongst others, refractories, foundry moulds, glaze opacifiers, the glass industry, abrasives, ceramics and ceramic colours, piezoelectrics, capacitors, pyroelectrics, solid electrolytes, the oil industry, wool flame-proofing and water-proofing, photography, the textile industry, medicine and cosmetics [1-8]. Zirconium's silicate salt is used for the immobilisation of wastes with actinides [8-10]. Most of these applications are related to zirconia, the oxide of zirconium IV.

Historically, zirconium did not receive much attention because it had few industrial applications in early times. Zircon[1], the main source of zirconium, was first known in zirconium compounds, as *hyacinth, jargon, jacinth, ligure, diamante brut or clarus hyalinus* in the Middle Ages [2, 3, 7, 11, 12]. The mineral is also mentioned in biblical writings. In addition, it was believed to be an imperfect diamond, called a *Matara Diamond* [1]. It was Werner who gave it the name zircon [7, 11].

In 1789, Klaproth fused zircon with sodium hydroxide and extracted the product with hydrochloric acid. In the solution, he found an element that exhibited novel behaviour [2, 12]. Berzelius was the first to extract zirconium, in 1824 [2, 12]. Lely and Hamburger prepared the first relatively pure zirconium, in 1904 [12]. Really pure zirconium was prepared only in 1925, by Van Arkel-De Boer using the iodide method [13].

Naturally occurring zirconium compounds contain small amounts of hafnium, about 2%. Their complete separation is very difficult due to their essentially identical atomic and ionic radii. This leads, essentially, to their having identical chemical properties [14]. There are only a few ores rich in hafnium, namely alvite, with 13.6%, and thortveitite, with 2.7% [13]. Ores with a zirconium content of more than 95% have been found associated with tantalum ore in Mozambique [12]. Ryshkewitch and Riecherson [5] reported ores with concentration runs of HfO_2 up to 22%. In most applications, zirconium chemicals can be used with their hafnium impurities. Ores with high levels of hafnium also have high levels of radioactive impurities [12]. The need to produce pure zirconium, for atomic application, and pure hafnium was the

[1] Mineral in which the major component is $ZrSiO_4$.

motivation for developing the extraction technology and this made possible the production of several zirconium chemicals [2, 12], of which zircon and zirconia were the first to find application [2].

1.1 Aim of the Study

There is an increasing demand for zirconium chemicals. Inexpensive methods for the recovery of zirconium and zirconium chemicals from the most abundant and cheapest source, zircon, need to be found and optimised.

Zircon is widely found all over the world in beach sands, which are constantly being formed. Beach sand is undoubtedly the most abundant and inexpensive raw material for zirconium and zirconium chemicals [2, 3, 12]. The major problem with zircon is its high chemical stability and the high level of impurities encaged in the structure. The chief impurities are iron, aluminium, silicon, nickel and titanium, apart from radioactive impurities such as uranium and thorium [2, 3, 5, 13, 15, 16].

The extreme chemical and thermal stability of zircon can be explained by the high coordination of bisdisphenoid ZrO_8 in a tetragonal structure with SiO_4 tetrahedra [10, 17]. Zircon therefore requires aggressive reaction conditions for decomposition [2, 6, 12]. Decomposition of zircon with alkali at high reaction temperatures is a well-known procedure [2, 6, 12, 15]. De Wet and his team have developed a novel process of recovering zirconia from zircon sands using this reaction. Compared with conventional processes, the De Wet process has the following advantages [3, 16]:

- Fewer process steps are needed to manufacture acid zirconium sulphate tetrahydrate (AZST)
- A comparatively low-cost pigment-suitable zirconia with reduced radioactivity content can be made.
- The alkali reactant can be recovered in the form of a saleable, radioactivity-free, sodium silicate product stream.
- Sulphuric acid is used in economical quantities in the manufacture of AZST; the overall process requires less than 5% stoichiometric excess of sulphuric acid.

- The radioactivity is leached out of a solid phase instead of using precipitation steps that require chemical additions and generate much waste.
- There are fewer effluent streams and less waste to discard.

In this study, a kinetic analysis was undertaken with the aim of optimising the recovery of zirconia during the alkali fusion step of the De Wet process, bearing in mind that zirconia can be utilised as a starter material for the production of other zirconia chemicals and that it is also the most important zirconium chemical.

The optimisation included determining the optimum fusion temperature, i.e. the temperature at which the conversion can be considered as maximum for the process, taking into consideration time and production costs. Secondly, the appropriate mol ratio for optimum conversion was sought. A constant guideline for this study was that an industrial process must be effective in terms of both time and costs.

1.2 Methodology

The research was undertaken at the Institute of Applied Materials, University of Pretoria, with financial support from the THRIP programme of the Department of Trade and Industry and the National Research Foundation (NRF) of South Africa, as well as from Kumba and Xyris Technology CC.

The main objective of the study was to optimise the alkali fusion step in the De Wet process. For that purpose, the research was divided into three different steps as follows:

- **Literature review**. Using existing facilities, conventional methods of recovering zirconia from zircon sands were reviewed. The aim here was to acquire knowledge of this specific problem, and how the research results could be applied to solving this problem.
- **Experimental step**. This consisted of practical laboratory work to obtain results.
- **Evaluation of the results**. The results obtained were assessed in relation to whether the research objectives had been achieved.