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OPTIMISATION OF ALKALI-FUSION PROCESS FOR ZIRCON SANDS:

A KINETIC STUDY OF THE PROCESS

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ABSTRACT

Zirconium chemicals are attracting increasing interest owing to the growing number of applications for speciality chemicals and the low toxicity of zirconium chemicals. Currently, the main source of zirconium chemicals is zircon. Zircon beneficiation is complex due to its high thermal and chemical stability. Zircon also contains radioactive impurities caged in its structure. In classic methods, these impurities are removed by means of various precipitation processes, which are reportedly both time-consuming and inefficient. The De Wet process represents an improved zirconium chemicals recovery process that starts from zircon. In this approach, the radioactivity is effectively and efficiently leached from a solid phase.

The present study was, however, concerned primarily with the optimisation of the alkali fusion step in the De Wet process of zirconia and zirconium chemicals recovery. For this purpose, fusions were conducted using varying fusion temperatures, reaction times and reagent ratios. Fusion times were varied from 1 to 336 hours at temperatures from 600 to 850 °C. Stoichiometric ratios ranging from 1 to 6 mols of sodium hydroxide per mol of zircon were investigated.

The 336-hour fusions were used to identify the equilibrium phases that form at each temperature. Below 650 °C, only sodium zirconate (Na_2ZrO_3) is observed in the reaction mixture. Above 700 °C, sodium zirconium silicate (Na_2ZrSiO_5) is also present in the product spectrum. The relative abundance of these two zirconium chemicals is dependent on the stoichiometry. Below 2 mols of sodium hydroxide, sodium zirconium silicate is virtually the sole phase that forms. Above this level, the sodium zirconate content increases with the amount of sodium hydroxide per mol of zircon. At 6 mol of sodium hydroxide, it is the only zirconium-containing phase observed.

Both equilibrium compounds can be used to recover zirconia. Sodium zirconate requires more base for its formation, but hydrolyses efficiently in water to hydrous zirconia. This allows the recovery of the alkali reagent as a saleable product stream. The formation of sodium zirconium silicate consumes only half the amount of base required for sodium zirconate. However, it is insoluble in water and hydrolyses only in acid media. Thus its presence in the fusion product leads to reduced alkali recovery, increased acid reagent consumption and higher volumes of salt waste.

From a practical point of view, short fusion times are preferred and are also more cost-effective. The zirconia yield showed a temporal maximum at 2-hour fusions. With this fusion time, optimum recovery of zirconia, as well as salt waste minimisation, was achieved by fusing at 850 °C in a 2:1 reagent mol ratio mix.

Impure zirconia can also be obtained directly by calcining the solid residue that remains after the following sequence of steps: fusion, water leach, dilute acid hydrolysis and, finally, water wash. A product containing 79% zirconia was obtained in this way after fusing for 8 hours at 850 °C with a 4:1 mol ratio.

OPSOMMING

Sirkoniumchemikalië lok toenemende belangstelling as gevolg van nuwe toepassings in spesialiteitschemikalieë en die lae giftigheid van sulke verbindings. Die hoofbron vir sirkoniumchemikalië is tans sirkoon. Die hoë termiese en chemiese stabiliteit van sirkoon bemoeilik egter chemiese opgradering. Sirkoon bevat ook radioaktiewe onsuiwerhede in sy struktuur. In die klassieke herwinningsmetodes word hierdie onsuiwerhede verwyder deur middel van duur en tydrowende presipitasieprosesse. Die De Wet proses behels 'n verbetering op die bestaande sirkoonherwinningsprosesse. In hierdie proses word die radio-aktiwiteit effektief en kostedoeltreffend vanuit 'n vastestoffase uitgeloog.

Hierdie studie was egter hoofsaaklik gemoeid met die optimisasie van die alkali-smeltingsstap in die De Wet proses vir die herwinning van sirkoniumchemikalieë. Vir hierdie doel is alkali-fusie by verskillende temperature, reaksietye en reagensverhoudinge uitgevoer. Fusietye is gevariëer van 1 tot 336 ure by temperature van 600 tot 850 °C. Stoïgiometriese verhoudings vanaf 1 to 6 mol natriumhidroksied per mol sirkoon is ondersoek.

Die 336-uur smeltings is gebruik om die ewewigsreaksieprodukte by verskillende temperature te identifiseer. Daar is gevind dat onderkant 650 °C natriumsirkonaat (Na_2ZrO_3) as die enigste sirkoniumproduk in the reaksiemengsel vorm. Bokant 700 °C vorm natriumsirkoniumsilikaat (Na_2ZrSiO_5) as tweede produk. Die relatiewe verhouding van hierdie twee produkte in die hoë-temperatuursmeltsel is afhanklik van reagensstoïgiometrie. Wanneer dit onder 2 mol natriumhidroksied per mol sirkoon is, vorm slegs natriumsirkoniumsilikaat. Bokant hierdie vlak vorm daar wel ook natriumsirkonaat. Met 6 mol natriumhidroksied per mol sirkoon, is laasgenoemde die enigste sirkoniumbevattende produk wat vorm.

Beide reaksieprodukte is geskik vir die herwinning van sirkoniumchemikalieë vanaf sirkoonsand. Natriumsirkonaat benodig 'n groter hoeveelheid van die reagens maar dit hidroliseer geredelik in water om 'n neerslag van sirkoniumhidroksied te vorm. Dit vergemaklik die herwinning van die alkalië in die vorm van 'n verkoopbare natriumsilikaatproduk. Die vorming van natriumsirkoniumsilikaat verg minder natriumhidroksied. Die produk is egter nie oplosbaar in water nie en sure word benodig om dit te hidroliseer en die sirkonia vry te stel. Dus sal die teenwoordigheid daarvan in die

reaksieproduk lei tot verminderde alkaliherwinning, groter verbruik van suur veroorsaak en ook lei to hoër volumes van die soutafvalstroom.

In die praktyk word kort fusietye verkies wat ook kostebesparing teweeg bring. Die sirkoniaherwinning wys ‘n tydelike maksimum by die 2-uur punt. By hierdie fusietyd gee ‘n reaksietemperatuur van 850 °C en ‘n 2:1 reagensmolverhouding optimale herwinning van sirkonia en minimale soutvorming.

Onsuiwer sirkonia kan ook direk vanaf die fusieproses verkry word deur kalsinering van die vastestofresidu na die volgende prosesstappe: waterloging, suurhidrolise en waterwas. ‘n Produk wat 79% sirkonia bevat is verkry na fusie vir 8 uur by 850 °C en ‘n 4:1 stoïgiometriese molverhouding.

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