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# **PROCESS DEVELOPMENT FOR THE PRODUCTION OF BENEFICIATED TITANIA SLAG**

by

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# PROSESONTWIKKELING VIR DIE PRODUKSIE VAN OPGEGRADEERDE TITAAN SLAK

deur

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Vir die graad Philosophiae Doctor aan die Departement Materiaalkunde en  
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## OPSOMMING

Daar is 'n reeks voermateriale beskikbaar vir die produksie van  $\text{TiO}_2$  pigment. Dit wissel van natuurlike voermateriale soos ilmeniet en rutiel to sintetiese rutiel. Daar is 'n sterk toename in die prys van titaanryke voermateriale soos die  $\text{TiO}_2$  graad van die materiale toeneem. 'n Proses is ontwikkel om voordeel te trek uit die prysverskil tussen chloriedgraad slak en natuurlike rutiel. Die proses verhoog die  $\text{TiO}_2$  inhoud van die slak van ~85% na meer as 95%. Hierdie "beneficiated titania slag" (BTS) lyk na 'n ideale voermateriaal vir die chloried proses.

Aanvanklik is verskeie prosesse geëvalueer. Daar is veral klem gelê op die voorafbehandeling van die slak. Dit was nodig omdat die onsuiverhede in slak baie moeilik loog. Deur van 'n geskikte voorafbehandeling gebruik te maak kan die onsuiverhede maklik loogbaar gemaak word, terwyl die titaan grootliks nie-loogbaar bly. Die resultate het getoon dat 'n proses wat uit oksidasie- en reduksie roosting bestaan gevolg deur loging, die grootste kans op sukses het.

Die eerste deel van die prosesontwikkeling is in 'n steenkoolgevuurde fluidbedrooster gedoen. Die prosesparameters was gedeeltelik geoptimeer, omdat daar kon slegs BTS met 'n  $\text{TiO}_2$  inhoud van 94% gemaak kon word. Die daaropvolgende prosesontwikkeling is in 'n klein roostereaktor gedoen wat gekoppel was aan 'n gasmengstelsel. Dit het beter beheer oor die roostertoestand toegelaat. Die proses parameters is hiermee geoptimeer na: oksidasie by 850 °C vir 1.5 h in 8%  $\text{O}_2$ ; reduksie by 850 °C vir 10 min in 100% CO en loging in 20% kokende soutsuur. Onder hierdie prosesondisies is BTS met 'n graad van > 97%  $\text{TiO}_2$  geproduseer.

# PROCESS DEVELOPMENT FOR THE PRODUCTION OF BENEFICIATED TITANIA SLAG

by

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## ABSTRACT

There is a range of feed materials available for the production of TiO<sub>2</sub> pigment. These range from natural materials like ilmenite and rutile to synthetic materials like synthetic rutile. There is a large increase in the price of titaniferous feed materials as the TiO<sub>2</sub> content of the material increases. To take advantage of the difference in price between chloride grade slag and natural rutile a process was developed to increase the TiO<sub>2</sub> content of chloride grade slag from ~85% to more than 95%. This beneficiated titania slag product (BTS) should be ideal as feed material to the chloride pigment process.

Initially several processes were evaluated. Particular emphasis was placed on the slag pre-treatment procedure. This was necessary as impurities could only be leached with difficulty from as-cast slag. A suitable pre-treatment procedure would render the impurities easily leachable, while the titanium is retained in an insoluble form. The results indicated that a process consisting of oxidation and reduction roasting would satisfy these requirements.

Detailed process development was then undertaken on this process. The first phase of the process development was conducted in a coal fired fluid bed roaster. This allowed a set of semi optimised process parameters to be established, but the highest TiO<sub>2</sub> content that could be achieved was 94%. A second stage of process development was under taken under more controlled conditions, using a small fluid bed reactor connected to a gas mixing system. Based on the results in this phase of the process development a new set of optimum process parameters was established. They are oxidation at 850 °C for 1.5 h in an atmosphere containing 8% O<sub>2</sub>; reduction at 850 °C for 10 min in a 100% CO atmosphere and leaching in boiling 20 % hydrochloric acid for 12 h. Under these conditions it was possible to produce BTS containing > 97% TiO<sub>2</sub>.



During oxidation of titania slag several important morphological changes occur. These are the conversion of the original  $M_3O_5$  phase in the slag to a mixture of rutile/anatase, hematite and ferric  $M_3O_5$ . In the process the iron in the slag migrates to the outside surfaces of the slag particles where it is easily accessible during leaching. The iron containing phases are converted to ilmenite during reduction and during leaching the ilmenite is removed. This yields the BTS product. As the oxidation roast appeared to be a very important of the BTS process it was decided to investigate the mechanism of titania slag oxidation. A mechanism based on the nucleation energy that is required to form the relevant phases during oxidation was proposed. This mechanism was tentatively confirmed through selected experiments.