

4. PROCESS DEVELOPMENT PHASE 2

4.1 Introduction

Phase 1 of the process development for the production of BTS was conducted with a coal fired fluid bed roaster. This did not allow close control over parameters such as oxygen potential. The aim of the second phase of the process development was to refine the roast conditions necessary for the production of BTS with a 95 % TiO₂ content. The previous work showed that oxidation was the most critical part of the BTS process. The bulk of the work during this phase was therefore concentrated on oxidation of standard titania slag. Some experiments were also conducted on high iron titania slag as the high iron content magnifies the mechanisms that operate during roasting.

4.2 Experimental design

4.2.1 Feed material

The slag used for this investigation was obtained from the 6th IHM 3MVA plasma furnace campaign of July 1997. The complete analyses are listed in Appendix VII. Table 33 shows the concentration of selected elements in the feed slag. For the purposes of this investigation the feed slags were placed in two categories based on their chemical composition namely standard slag and high iron slag. Table 34 gives the phase composition of the slag as determined by XRD.

Table 33. Chemical composition of the feed slags used in this investigation.

PFE no.	Classification	TiO ₂ %	Ti ₂ O ₃ %	Fe %	FeO %	Fe ₂ O ₃ %
469	standard	52.3	32.1	0.03	9.3	-
437	high iron	58.40	13.60	-	21.90	-

Table 34. Phase-chemical composition of the feed slags used in this investigation.

PFE no.	Classification	Major Phases	Minor Phases	Trace Phases
469	Standard	FeTi-Oxide	-	Rutile
437	High iron	FeTi-Oxide	-	Ilmenite, Iron

Legend: FeTi-Oxide – M₂O₃ solid solution; Rutile – TiO₂; Ilmenite – FeTiO₃

4.2.2 Experimental plan

In previous investigations it was shown that oxidation is the most important stage of the process for the production of BTS. Therefore it was decided to focus on investigating variables that have an influence on this process stage. To evaluate the effectiveness of the oxidation roast it was decided to subject most of the samples to a standard reducing roast and leach procedure. This procedure was only modified in the case of the reduction time investigation where a standard oxidation roast and leach procedure were used. The final TiO₂ content or the amount of iron extracted from the slag after leaching was used as an indication of the effectiveness of the oxidation roast. The following parameters were investigated:

- Oxidation atmosphere;
- Oxidation temperature;
- Oxidation time;
- Reduction time and;
- Particle size.

The experimental plan was designed to investigate the effect of all the above-mentioned parameters on the standard slag, but the effects of only some of them were evaluated for the high iron slag. A list of all the experiments that were conducted on the various feed slags is given in Appendix VIII.

4.2.3 Experimental procedure

4.2.3.1 Roast procedure

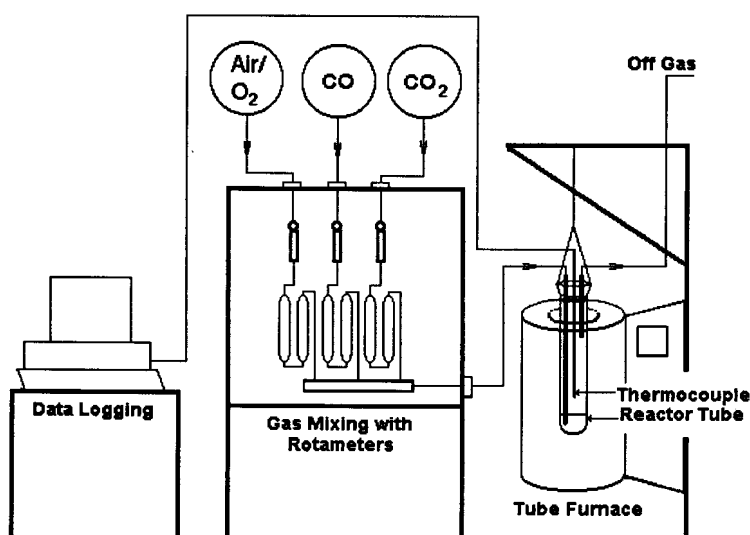


Figure 26. Experimental set-up used for the roast experiments.

Roasting was conducted in a small fluid bed roaster. The set-up consisted of a 20 mm diameter glass reactor, a tube furnace and a gas mixing system (Figure 26). The feed material was titania slag, separated in several narrow size fractions. About 20 – 50 g slag was loaded into the reactor before each experiment. The gas mixing system was then used to provide the oxidation atmosphere inside the reactor with air, carbon dioxide, oxygen or mixtures of these gases. The flow rates of the gases were controlled with rotameters to a total flow of 11 L/min at 20 °C. This flow rate was selected after the minimum and maximum gas flow rates for fluidisation were calculated (Appendix XIII).

The experiment started as soon as the reactor was lowered into the pre-heated tube furnace. The temperature inside the fluidised bed was measured with a thermocouple. The temperature inside the fluid bed initially increased sharply by about 150 to 200 °C, but it started to decline after about 5 min. After about 10 min the

bed temperature was within 5 °C of the target value and it remain there for the duration of the experiment. After the oxidation roast the experiment was either stopped and cooled to room temperature, to allow a sample to be taken, before the reduction roast, or the oxidation gases were directly changed to carbon monoxide gas. Previous experiments had indicated no noticeable difference in the roasting behaviour of titania slag between experiments that were interrupted after oxidation (with cooling to room temperature) and experiments where no interruption occurred. Once the reducing roast was finished the reactor was removed from the furnace and allowed to cool in air. The slag sample was then removed from the reactor. Part of the sample was submitted for chemical and mineralogical analysis and the rest of the slag sample was subjected to a leach experiment.

4.2.3.2 Leach procedure

Leach experiments were conducted in 2 L Erlenmeyer flasks fitted with reflux condensers. The purpose of the condensers was to limit evaporation losses. The reactors were placed on a hot plate that kept the leach solution at boiling point. No additional stirring was provided. The concentration of the feed solutions was 20 weight % hydrochloric acid. The reactor was filled with 0.5 L solution and once boiling point was reached about 15-30 g dry roasted feed material was charged. Pulp samples were taken at timed intervals, filtered and reserved for chemical analysis. The experiments were stopped after 12 h. The intermediate and final solution samples were submitted for a complete chemical analysis. At the end of the leach the slurry was filtered and repeatedly repulped and washed until the pH of the wash water was neutral. Special care was taken to limit losses of solids during the bulk filtration and washing operations. The filter cake was dried at 110 °C overnight, weighed and submitted for full chemical analysis.

4.2.3.3 Electron microprobe analysis procedure

Selected slag samples were mounted in resin before they were mechanically ground and polished to a surface roughness of around 1 µm. An optical microscope was then used to select three particles in each sample for analysis. The positions of the selected particles were marked with a diamond tip marker and a layer of carbon was deposited onto the polished blocks to prevent the build up of an electrostatic charge on the surface during analysis. Following this, the coated samples were placed into an electron microprobe (ARL SEMQ-37) fitted with a wavelength dispersive spectrometer (WDS). Thereafter the marked particles were located with an optical microscope fitted to the microprobe and their positions were stored on a computer. The microprobe then performed a series of point chemical analysis on each of the marked particles, starting at the outside surface and moving to the centre in 5 µm intervals. The electron beam that was used had a spot size of 1 to 3 µm, while the operational accelerating voltage was 15 kV and the beam current was 0.03 µA. Each analysis took approximately 20 s to complete.

4.2.3.4 Mössbauer analysis procedure

^{57}Fe Mössbauer-effect spectroscopy (MES) is a (nuclear) γ -radiation resonance technique involving the recoil-free emission of probing radiation by the source and the subsequent recoil-free absorption of this γ -radiation by ^{57}Fe nuclei in the absorber i.e. sample of interest. As such it is extremely sensitive to the local surroundings of ^{57}Fe atoms; these have a 2% natural abundance and are therefore present in all iron-bearing compounds. The local surroundings of the iron nuclei are primarily constituted by the electronic structure of the Fe atom, the compositional make-up of neighbouring atoms and by neighbouring defect structures. Therefore in the case of iron-bearing compounds the local-probe nature of the technique makes it a powerful non-destructive analytical tool for, establishing the oxidation state of iron (e.g., ferrous or ferric), quantifying the abundance's of different iron compounds within the same sample (i.e., phase analysis) and establishing the overall crystal chemistry when used in conjunction with complementary techniques like XRD and SEM. Typically iron-phase abundance's to as low as 5% may be detected with high accuracy. Moreover, as an atomic-scale local probe it is equally effective in the analysis of poorly crystallised or amorphous materials where conventional macroscopic-type probes like XRD have considerable limitations. The spectral parameters that serve as fingerprints in conventional transmission MES are the, isomer shift δ , quadrupole splitting Δ and internal magnetic field B_{hf} , all of which serve to characterise the chemical state of Fe in the solid phase.

The titania slag samples were prepared by milling it to a fine powder. MES measurements were conducted at room-temperature in the conventional transmission geometry using a 5-10 mCi $^{57}\text{Co}(\text{Rh})$ radioactive Mössbauer source. Typically 40-50 mg/cm^2 of sample was used, corresponding to 5-10 mg/cm^2 of Fe. This is considered to be an optimal thickness to avoid spectral lineshape distortions, ensure acceptable (i.e., at least 30 %) transmission of the incident radiation when taking into consideration electronic absorption effects, and to have adequate quantities of the ^{57}Fe isotope in the sample to ensure a satisfactory signal-to-noise ratios after typical 12-24 hour data accumulation periods. Some samples showed evidence of very low iron content in which case data accumulation was extended for 3-4 days to obtain an adequate signal-to-noise ratio for a reliable analysis. Data analysis was effected by using the non-linear least squares Mössbauer analysing programme NORMOS (supplied by WISSEL Starnberg-Germany) using a minimum number of spectral components, each having a Lorentzian lineshape. Final parameters of the fitted components were compared with the accepted literature values for various iron-oxides and iron-titanium-oxides to make a phase identification. Oxidation states of Fe in the various phases were unambiguously determined from the combination of values of fitted δ and Δ parameters obtained for quadrupole doublets or from the B_{hf} value of magnetically split sextets.

4.3 Results and Discussion

4.3.1 Standard titania slag

4.3.1.1 Oxidation

The effect of oxidation time

The main purpose of the oxidation roast is to oxidise all the easily leachable Ti(III) in the slag to largely insoluble Ti(IV). During this procedure all the Fe(II) that is present in the slag is oxidised to Fe(III). The effect of oxidation on the slag was studied by varying the duration of the oxidation roast from 0.5 to 8 h. Table 35 gives the phase-chemical composition of the samples after oxidation. This shows that the amount of M_3O_5 in slag declines and the amount of rutile increases with an increase in oxidation time. Traces of anatase are present in all the samples.

Table 35. The phase-chemical composition, as determined by XRD, of standard slag after oxidation. The samples are categorised by the oxidation time used. For the experiments listed the slag was oxidised at 850 °C in 8 % O_2 .

Phase composition after oxidation		Major Phases	Minor Phases	Trace Phases
Sample	PFE			
0.5 h	1172/1382	FeTi-Oxide	Rutile	Anatase
1 h	1173/1383	FeTi-Oxide; Rutile	-	Anatase
2 h	986/1375	Rutile; FeTi-Oxide	-	Anatase
3 h	1384	Rutile	FeTi-Oxide	Anatase
4 h	1174/1377	Rutile	FeTi-Oxide	Anatase
8 h	1378	Rutile	FeTi-Oxide	Anatase

Legend: FeTi-Oxide – M_3O_5 solid solution; Rutile – TiO_2 ; Anatase – TiO_2 ; Ilmenite – $FeTiO_3$; Iron – Fe^0

An optical and SEM investigation of the samples revealed that oxidation proceeded in a shrinking core fashion. The slag samples oxidised for 0.5 and 1 h (Figures 27 and 28) contained many particles with a zoned appearance. The cores of the particles were still unreacted and appeared relatively dense, but in the vicinity of cracks passing through the cores metallic iron particles were visible in association with rutile. The unreacted cores were surrounded by oxidised zones: These mantle zones were slightly porous and enriched in TiO_2 . Another zone could be distinguished on the outsides of the particles. This outer shell was characterised by a very high concentration of iron. The slag samples oxidised for 2 and 3 h (Figure 29) appeared slightly different from the slag oxidised for shorter periods. The majority of the particles were completely oxidised, but some of the coarser-grained particles had small, unreacted, M_3O_5 cores. The slag particles were in general slightly porous with iron-enriched rims. All the slag particles appeared to be completely oxidised after 4 and 8 h (Figure 30). Optically no particles with unreacted M_3O_5 -cores could be recognised. Fine pores were present throughout the majority of slag particles. Some particles, however, had a dense appearance. This was accompanied by the presence of mainly anatase in the centres of the individual slag particles. Rutile was in general abundant in the mantle zones and outer margins of the slag particles as well as being associated with cracks extending through the particles. There were also particles with well-defined rutile-rich outer rims. From the chemical composition profiles it is clear that almost all of the iron had migrated to the outsides of the particles and that the cores consisted of almost pure TiO_2 .

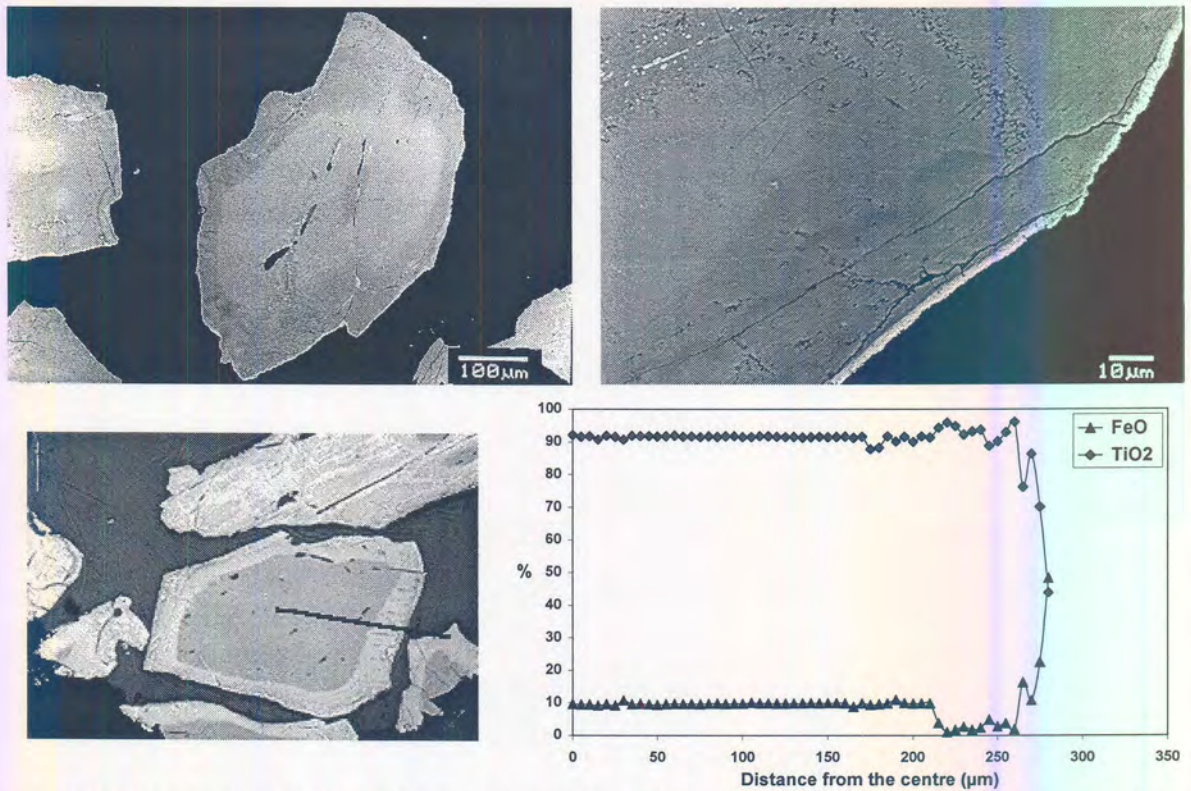


Figure 27. Standard titania slag oxidised for ½ h at 850 °C in 8 % O₂. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

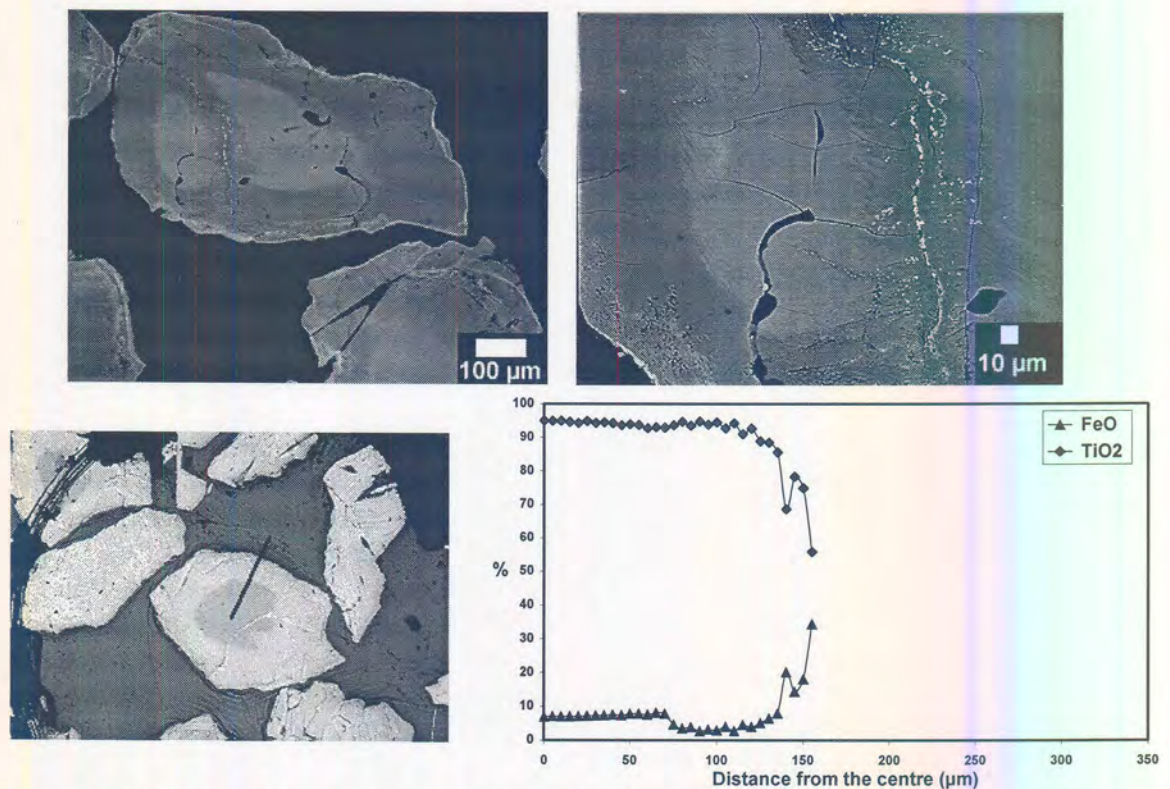


Figure 28. Standard titania slag oxidised for 1 h at 850 °C in 8 % O₂. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

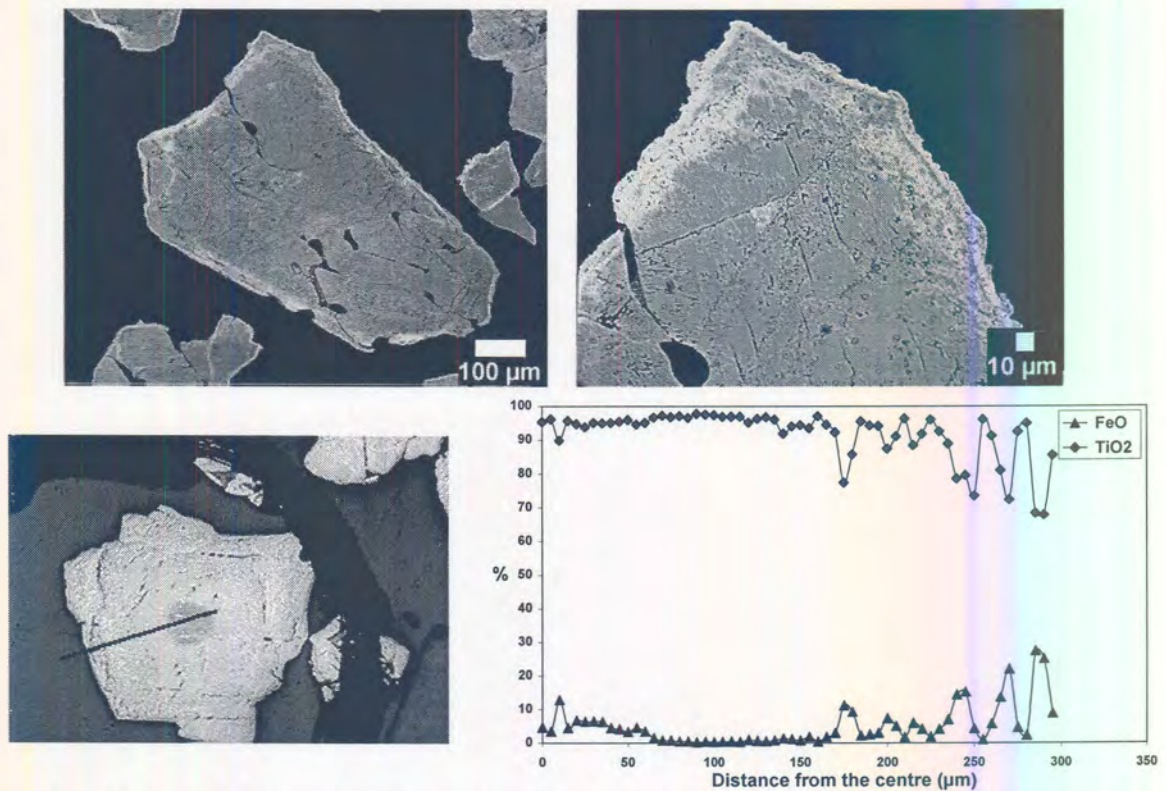


Figure 29. Standard titania slag oxidised for 2 h at 850 °C in 8 % O₂. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

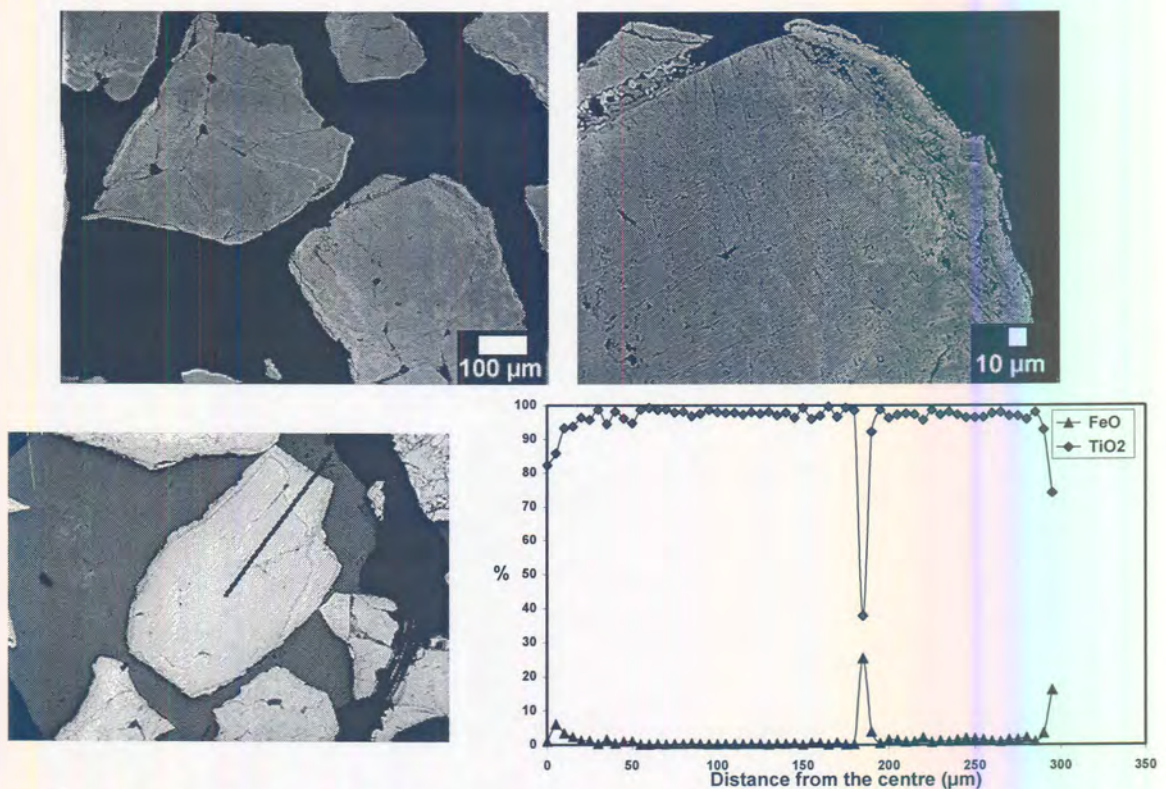


Figure 30. Standard titania slag oxidised for 4 h at 850 °C in 8 % O₂. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

During reduction no dramatic structural changes occurred in the slag, but an important phase change took place. Table 36 shows that ilmenite formed. The optical and SEM investigation indicated that the ilmenite formed in the areas of high iron concentration, on the rims of the particles (Figure 31). It is important to note that not all of the iron was converted to ilmenite and that some of the iron remained in the M_3O_5 phase in the unreacted cores of the particles, as indicated by XRD.

Table 36 The phase-chemical composition, as determined by XRD, of standard slag after oxidation and reduction. The samples are categorised by the oxidation time used. For the experiments listed the slag was oxidised at 850 °C in 8 % O_2 and reduced in 100 % CO for 20 min

Phase composition after reduction		Major Phases	Minor Phases	Trace Phases
Sample	PFE			
0.5 h	1421	FeTi-Oxide; Rutile	-	Ilmenite; Anatase
1 h	1427	Rutile; FeTi Oxide	Anatase	Ilmenite
2 h	1356	Rutile	FeTi-Oxide	Ilmenite; Anatase
3 h	1433	Rutile	-	FeTi-Oxide; Ilmenite; Anatase
4 h	1362	Rutile	-	FeTi-Oxide; Ilmenite; Anatase
8 h	1368	Rutile	-	FeTi-Oxide; Ilmenite

Legend: FeTi-Oxide – M_3O_5 solid solution; Rutile – TiO_2 ; Anatase – TiO_2 ; Ilmenite – $FeTiO_3$; Iron – Fe^0

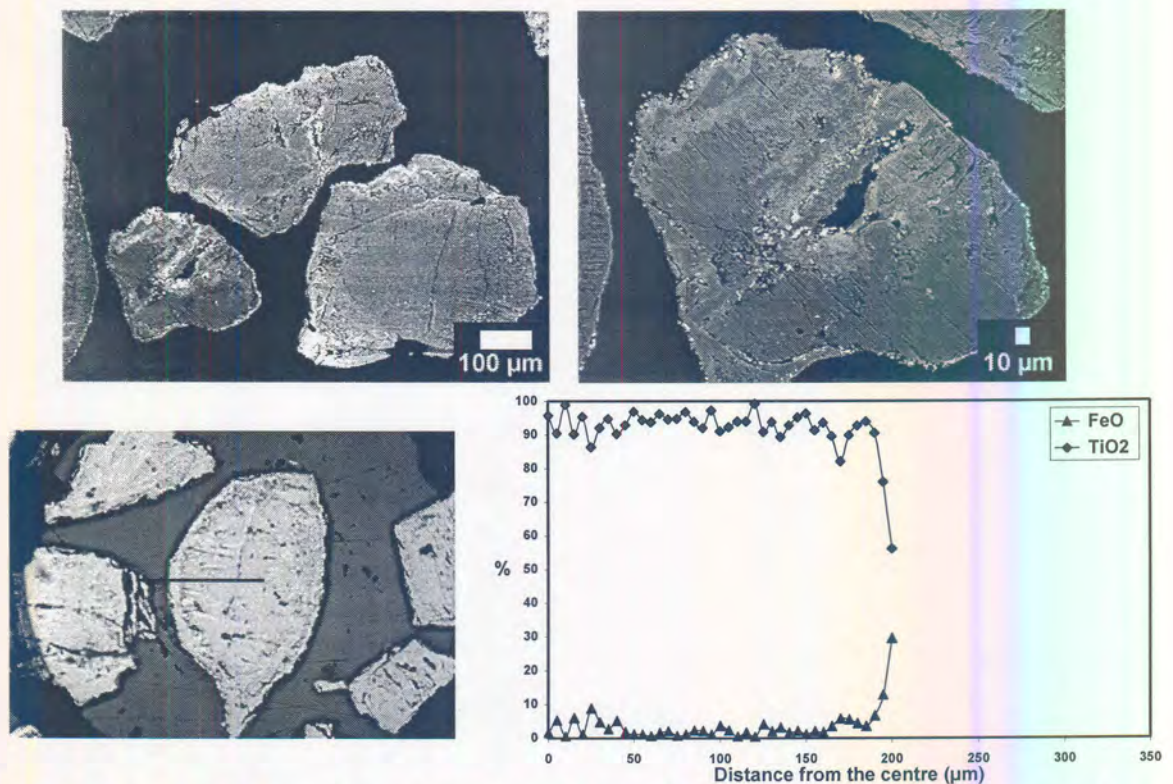


Figure 31. Standard titania slag oxidised for 2 h at 850 °C in 8 % O_2 and reduced for 20 min in 100 % CO. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

Table 37 gives the phase composition of the samples after oxidation, reduction and leaching. The absence of ilmenite suggests that ilmenite is the main phase that leaches, but the increase in the relative amount of anatase also suggests that some iron is leached from the M_3O_5 phase. The optical and SEM investigation showed that the particles became very porous during leaching (Figure 32), while the chemical

composition profiles indicates that most of the iron had been removed from the sample oxidised for 2 h.

Table 37. The phase-chemical composition, as determined by XRD, of standard slag after oxidation, reduction and leaching. The samples are categorised by the oxidation time used. For the experiments listed the slag was oxidised at 850 °C in 8 % O₂, reduced in 100 % CO for 20 min and leached in 20 % HCl for 12 h.

Phase composition after leaching		Major Phases	Minor Phases	Trace Phases
Sample	PFE			
0.5 h	1426	Rutile	Anatase; FeTi-Oxide	-
1 h	1432	Rutile	Anatase	FeTi-Oxide
2 h	1361	Rutile	Anatase	FeTi-Oxide
3 h	1438	Rutile	-	Anatase
4 h	1367	Rutile	Anatase	FeTi-Oxide
8 h	1373	Rutile	Anatase	FeTi-Oxide

Legend: FeTi-Oxide – M₃O₅ solid solution; Rutile – TiO₂; Anatase – TiO₂; Ilmenite – FeTiO₃; Iron – Fe⁰

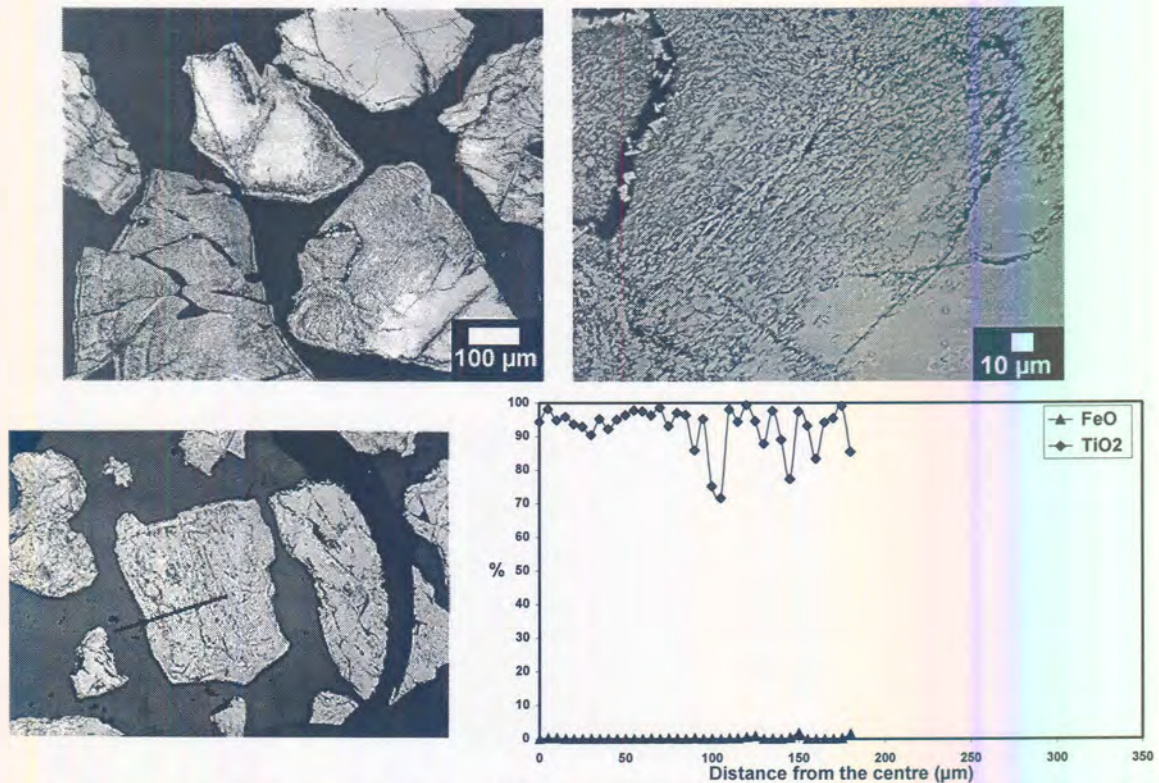


Figure 32. Standard titania slag oxidised for 2 h at 850 °C in 8 % O₂, reduced for 20 min in 100 % CO and leached for 12 h in boiling 20 % HCl. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

The sample oxidised for 0.5 h, reduced for 20 min in 100 % CO at 850 °C and leached for 12 h in boiling HCl had a weathered appearance but contained abundant particles with unaltered M₃O₅-cores. The outer margins appeared to be in general, relatively well leached and porous while the particles centres appeared to be unaffected. The finer-grained particles appeared to be more porous compared to the coarser-grained particles thus also slightly better leached. Fine metallic iron particles, associated with rutile along cracks extending through the slag particles, were still present and could be observed optically in some of the slag particles.

The samples oxidised for 1 and 2 h respectively, reduced in a 100 % CO atmosphere for 20 min at 850 °C and leached for 12 h in boiling HCl contained only a small number of slag particles with unreacted M_3O_5 cores. The slag particles displayed a weathered appearance and were porous due to leaching. The sample oxidised for 3 h; reduced in a 100 % CO atmosphere for 20 min at 850 °C and leached for 12 h in boiling HCl had a severely weathered appearance. The slag appeared porous but the porosity was concentrated at the outer rims and mantle zones of the individual slag particles.

The samples oxidised for 4 and 8 h respectively reduced in a 100 % CO atmosphere for 20 min at 850 °C and leached for 12 h in boiling HCl appeared to be completely leached; the majority of the particles had a severely weathered appearance. Slag particles displaying a relatively dense texture were also present. These dense particles consisted mainly of anatase.

Figures 33 and 34 show the effect of oxidation time on the final TiO_2 content of the slag and the percentage iron extracted during leaching. The log sheets of the experiments are given in Appendices IX to XII. Increasing the oxidation time from ½ to 3 h increased the iron extraction and the final TiO_2 content. This is probably a result of the decrease in the size of the unreacted M_3O_5 cores in the particles. When the slag is oxidised for more than 4 h the iron extraction and final TiO_2 content decreased slightly.

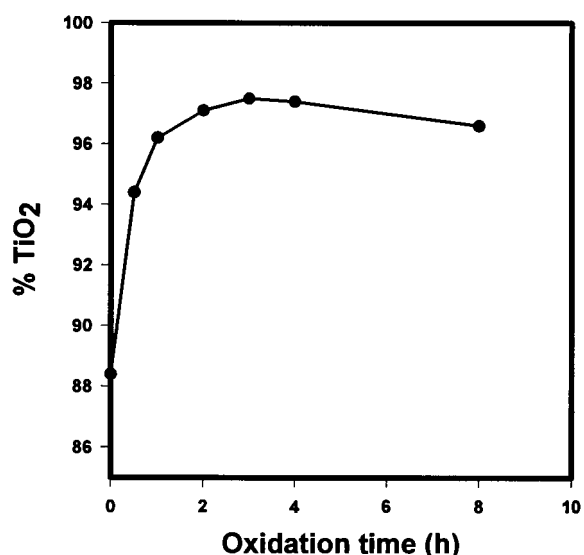


Figure 33. The influence of oxidation time during roasting of standard slag on BTS product grade. The slag was oxidised at 850 °C in 8 % O_2 , reduced in 100 % CO for 20 min and leached in boiling HCl for 12 h.

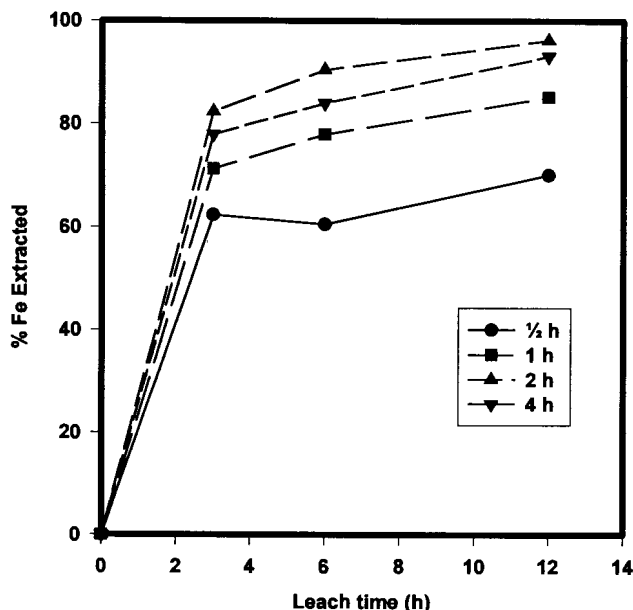


Figure 34. The influence of oxidation time, during roasting of standard slag, on iron extraction during leaching. The slag was oxidised at 850 °C in 8 % O₂, reduced in 100 % CO for 20 min and leached in boiling HCl for 12 h.

To quantify the phase changes that occur during oxidation a Mössbauer investigation was conducted (See Appendix XVIII). Standard titania slag was oxidised for different times at 850 °C in a 10 % O₂ atmosphere and characterised by XRD and Mössbauer spectroscopy. Table 38 shows the phase chemical composition of the samples. The results are similar to that of the oxidised samples presented in Table 35 except for the fact that more anatase seems to be present in these samples. The Mössbauer results indicated the presence of the ilmenite-hematite solid solution that were not detected by XRD; this is probably as a result of the fact that the concentrations of these phases were below the detection limit of the XRD technique. The Mössbauer results also differentiated between the two end members of the FeO.2TiO₂-Fe₂O₃.TiO₂ solid solution phase.

Table 38. Phase chemical analysis, as determined by XRD, of the oxidation samples used for the Mössbauer investigation.

Oxidised for:	PFE	Mineralogical composition		
		Main	Minor	Trace
0 min	-	FeTi-Oxide	Rutile	-
15 min	3060	Anatase, Rutile	Rutile, FeTi-Oxide	-
30 min	3061	Anatase, Rutile	FeTi-Oxide	-
60 min	3062	Anatase, Rutile	FeTi-Oxide	-
120 min	3063	Rutile, Anatase	FeTi-Oxide	-
240 min	3064	Rutile, Anatase	FeTi-Oxide	-

Legend: FeTi-Oxide – M₃O₅ solid solution; Rutile – TiO₂; Ilmenite – FeTiO₃; Iron – Fe⁰

The change in oxidation state of iron in the samples relative to the total amount of iron in the slag is presented in Figure 35. This shows that 95 % of the Fe(II) in the

slag is oxidised to Fe(III) after 2 h of roasting. The changes in the abundance of the iron bearing phases relative to each other are shown in Figure 36. This indicates that the $\text{FeO} \cdot 2\text{TiO}_2$ phase, originally present in the slag, is rapidly converted to $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$, the hematite-ilmenite solid solution phase. The ilmenite component of the M_2O_3 solid solution forms initially and then declines to zero after 60 min. The hematite part of the M_2O_3 solid solution also declines with increasing oxidation time, but a significant quantity was still present after 4 h.

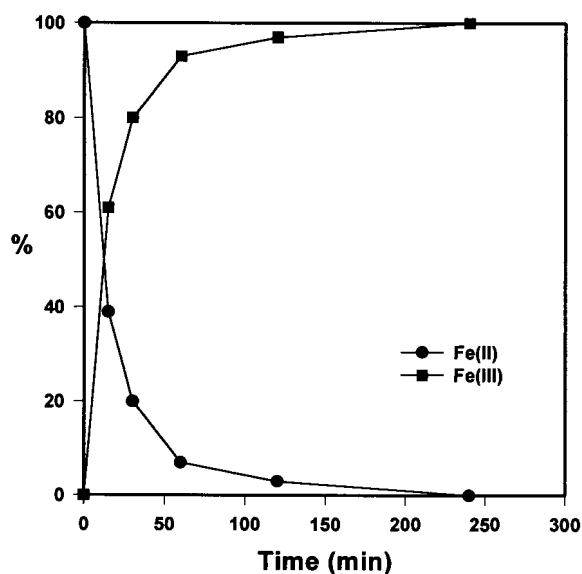


Figure 35. The change in the oxidation state of iron during oxidation roasting of standard titania slag as determined by Mössbauer analysis.

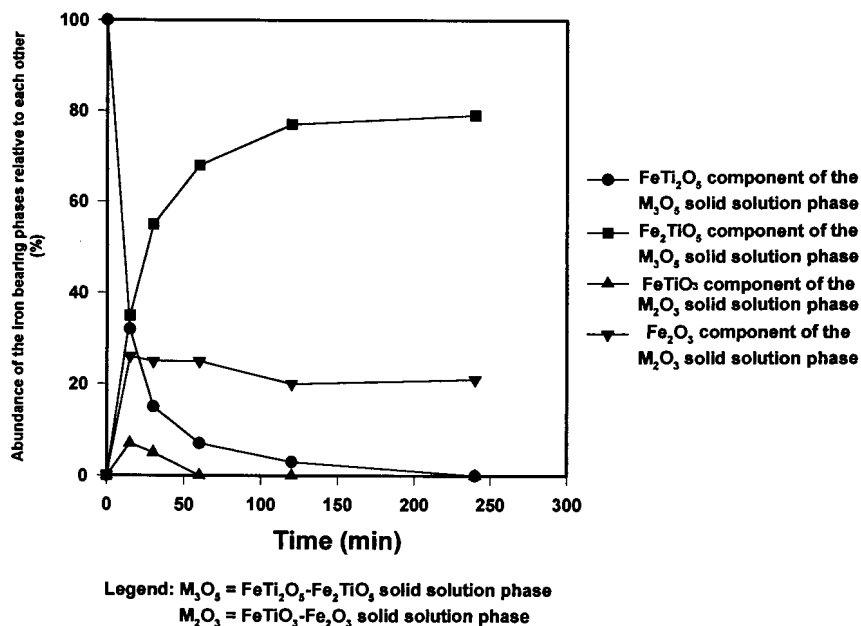


Figure 36. Changes in the relative concentration of the iron containing phases during oxidation roasting of standard titania slag as determined by Mössbauer analysis.

The effect of oxidation atmosphere and temperature

The final TiO_2 content of the slag and the iron extraction after leaching are also dependent on the oxidation atmosphere and the oxidation temperature. The influence of the oxidation atmosphere was evaluated by varying the oxygen content of the fluidising gas.

Table 39 shows the phases present in the slag after oxidation. This data indicates that the amount of M_3O_5 in the slag declines and the amount of rutile increases as the oxygen content of the gas during oxidation increases. It also indicates that the oxygen content of the oxidation gas influences the kinetics of oxidation. In an atmosphere containing 100 % CO_2 there is still a large amount of M_3O_5 left after oxidation, while in an atmosphere containing 4 % O_2 M_3O_5 is still a main phase in the oxidised product although more rutile than M_3O_5 is present in the slag. In samples oxidised in an atmosphere containing 8% or more O_2 the M_3O_5 phase is only present as a minor phase. Table 39 also shows that ilmenite formed during reduction along with some iron. The phase-chemical compositions of the leach residues indicates that ilmenite is removed during leaching. It also shows that the sample oxidised in CO_2 did not leach well as there was still a large amount of M_3O_5 present in the leach residue. In the other leach residues the M_3O_5 phase was relegated to a trace component. This suggests that the M_3O_5 phase is partially removed during leaching.

Table 39. The phase chemical composition as determined by XRD of standard slag after oxidation, reduction and leaching. The samples are categorised by the oxidation atmosphere that was used. The slag was oxidised at 850 °C for 2 h, reduced in 100 % CO for 20 min and leached in boiling 20 % HCl for 12 h.

Phase composition after oxidation		Main phases	Minor phases	Trace phases
Sample	PFE			
CO_2	985	FeTi-Oxide; Rutile	-	Anatase
4% O_2	988	Rutile; FeTi-Oxide	-	Anatase
8% O_2	986	Rutile	FeTi-Oxide	Anatase
12% O_2	987	Rutile	FeTi-Oxide	Anatase
21% (Air)	984	Rutile	FeTi-Oxide	Anatase
100% O_2	1499	Rutile	FeTi-Oxide	Anatase
Phase composition after reduction		Main phases	Minor phases	Trace phases
Sample	PFE			
CO_2	-	-	-	-
4% O_2	1052	Rutile	FeTi-Oxide	Ilmenite; Anatase; Iron
8% O_2	1356	Rutile	FeTi-Oxide; Anatase	Ilmenite
12% O_2	1047/1314	Rutile	FeTi-Oxide	Ilmenite; Anatase; Iron
21% (Air)	-	-	-	-
100% O_2	1469	Rutile	FeTi-Oxide	Ilmenite; Anatase; Iron
Phase composition after leaching		Main phases	Minor phases	Trace phases
Sample	PFE			
CO_2	1042	Rutile	FeTi-Oxide	-
4% O_2	1056	Rutile; Anatase	-	FeTi-Oxide
8% O_2	1046/1361	Rutile; Anatase	-	FeTi-Oxide
12% O_2	1051/1319	Rutile	Anatase	FeTi-Oxide
21% (Air)	1038	Rutile	FeTi-Oxide	Anatase
100% O_2	1474	Rutile; Anatase	-	FeTi-Oxide

Legend: FeTi-Oxide – M_3O_5 solid solution; Rutile – TiO_2 ; Anatase – TiO_2 ; Ilmenite – $FeTiO_3$; Iron – Fe^0

The influence of temperature was investigated by varying the roasting temperature between 750 °C and 950 °C. Table 40 gives the phase-chemical composition of the samples after oxidation, reduction and leaching. From this data it is clear that the kinetics of oxidation is influenced by roasting temperature. At 750 °C the oxidation of the M_3O_5 phase is only partially completed after 2 h, while it is substantially completed at 850 °C after the same time period. The amount of rutile relative to the amount of anatase in the slag also seems to increase as the roasting temperature increases. The presence of ilmenite in the reduced samples is once again shown in Table 40. No other major phase changes seem to have taken place during reduction. The phase composition of the leach residues also confirms that roasting temperature influences the kinetics of oxidation. In the samples oxidised at 750 °C and 800 °C there was still a large amount of M_3O_5 present that was not removed during leaching. There was no ilmenite present in the leach residues. It also seems that the amount of rutile relative to the amount of anatase increased as the roasting temperature increased.

Table 40. The phase-chemical composition as determined by XRD-analysis of standard slag after oxidation, reduction and leaching. The samples are categorised by the roasting temperature that was used. The slag was oxidised in 8 % O_2 for 2 h, reduced in 100 % CO and leached for 12 h in boiling 20 % HCl.

Phase composition after oxidation		Main phases	Minor phases	Trace phases
Sample	PFE			
750°C	981	FeTi-Oxide	Rutile	Anatase
800°C	-	-	-	-
850°C	986/1375	Rutile	Anatase; FeTi-Oxide	Iron
950°C	-	-	-	-
Phase composition after reduction		Main phases	Minor phases	Trace phases
Sample	PFE			
750°C	-	-	-	-
800°C	1403	FeTi-Oxide	Rutile	Anatase
850°C	1067/1356	Rutile; Anatase	FeTi-Oxide	Ilmenite; Iron
950°C	-	-	-	-
Phase composition after leaching		Main phases	Minor phases	Trace phases
Sample	PFE			
750°C	1026	FeTi-Oxide	Rutile	Anatase
800°C	1408	FeTi-Oxide	Rutile; Anatase	-
850°C	1046/1361	Rutile; Anatase	-	FeTi-Oxide
950°C	1071	Rutile	-	FeTi-Oxide

Legend: FeTi-Oxide – M_3O_5 solid solution; Rutile – TiO_2 ; Anatase – TiO_2 ; Ilmenite – $FeTiO_3$; Iron – Fe

The influence of the oxygen content of the oxidation atmosphere and the roasting temperature on the final TiO_2 content and the amount of iron extracted during leaching are shown in Figures 37, 38 and 39. The log sheets of the experiments are given in Appendices IX to XII. The oxygen content of the oxidation gas was varied by mixing air and CO_2 .

Figures 37, 38 and 39 show that the final TiO_2 content and the iron extraction are influenced by the roasting temperature and the oxygen content of the oxidation atmosphere. When roasting is performed in CO_2 the kinetics of oxidation is very slow as a result of the kinetics of the CO_2 dissociation reaction on the surface of the particles (Abuluwefa, et al., 1997). This results in a low iron extraction and a low final TiO_2 content in the slag. In air/ CO_2 mixtures with an oxygen content between 4 % and 12 % O_2 the kinetics of oxidation improves dramatically and the iron extraction and final TiO_2 content of the slag are much higher than for slag oxidised in CO_2 . The

effect of oxidation for 2 h appears to be very similar at 750 °C, 800 °C and 850 °C. In this temperature range the final TiO₂ content generally increases with a increase in the roasting temperature. There also appears to be an optimum oxygen concentration in this temperature range between 4 % and 8 % O₂. This optimum is much sharper at 800°C, in terms of the final TiO₂ content, than it is at 750 °C and 850 °C. This behaviour is unexpected as the difference between the PO₂ of a gas mixture containing 8% O₂ and air containing 21 % O₂ is very small. This suggests a kinetic effect – rather than an equilibrium one – in the achievement of the optimal structure during oxidation for subsequent removal of iron. This possible effect is discussed further in Chapter 5.

When the iron extraction curves in Figure 39 are considered the similarity between the curves at 750°C, 800°C and 850°C is also apparent. There is a very high initial rate of iron extraction up to 2 h of leaching followed by a sharp decline in the rate of leaching. The apparent optimum at oxygen concentrations between 4 % and 8 % O₂ is not as evident from the iron extraction curves, but there does appear to be a larger variation in the final amount of iron extracted between samples oxidised in the various gas mixtures at 800 °C versus the other roasting temperatures.

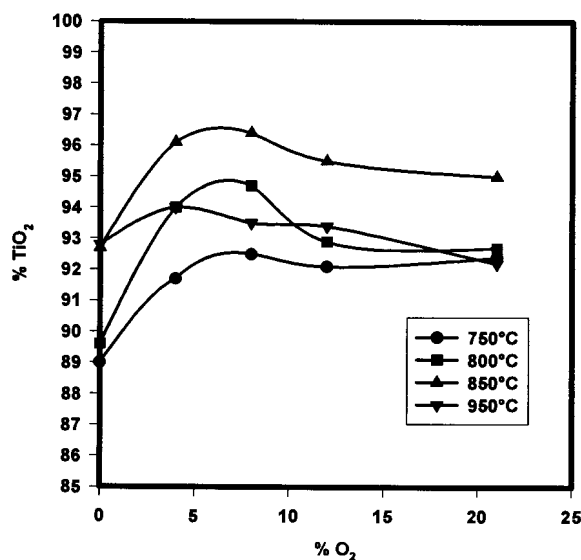


Figure 37. The influence of oxygen concentration and temperature during oxidation of standard slag on BTS product grade. The slag was oxidised for 2 h, reduced for 20 min in 100 % CO and leached for 12 h in boiling 20 % HCl. The slag contained the equivalent of 85% TiO₂ before treatment.

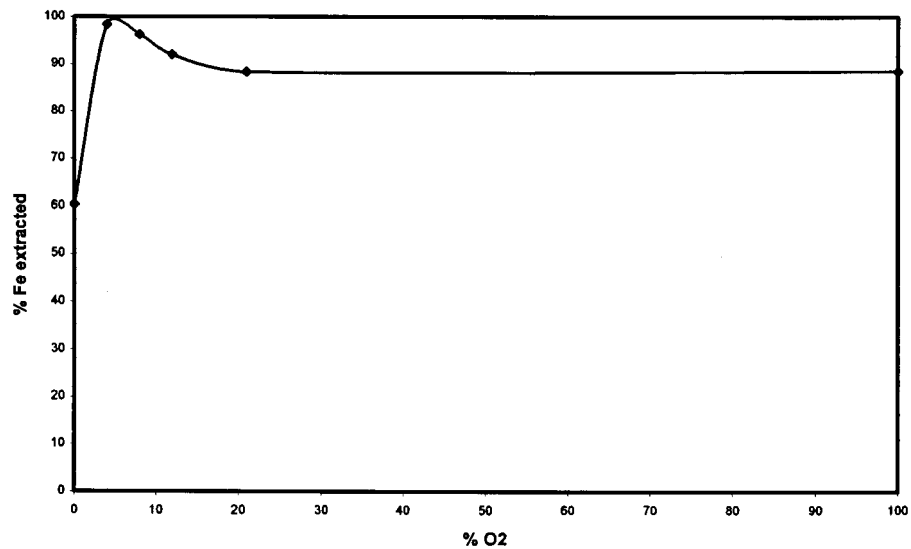


Figure 38. The influence of oxygen concentration during oxidation of standard slag at 850 °C on the total iron extraction during leaching. The slag was oxidised for 2 h, reduced for 20 min in 100 % CO and leached for 12 h in boiling 20 % HCl.

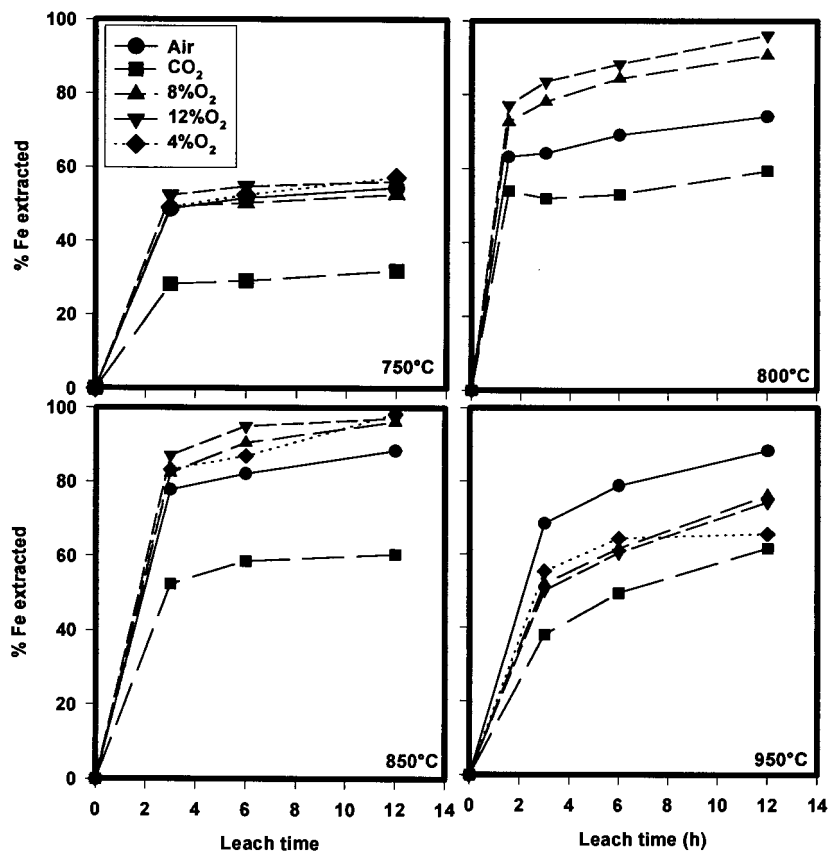


Figure 39. The influence of roasting temperature and oxygen concentration during oxidation of standard slag on the rate of iron extraction during leaching. The slag was oxidised for 2 h, reduced for 20 min in 100 % CO and leached for 12 h in boiling 20 % HCl.

At 950°C the oxidation behaviour changes dramatically as the final TiO₂ content and iron extraction decrease sharply relative to slag oxidised at 850 °C. The leach curves of slag roasted at 950 °C also differ from slag roasted at lower temperatures. The initial rate of iron extraction is still high, but it is lower compared to slag roasted at 850 °C and this is followed by a gradual decline in the rate of iron extraction after 2 h of leaching.

4.3.1.2 Reduction

Oxidised titania slag contains iron in the Fe(III) form. Iron in this form is notoriously difficult to leach and as a result the slag is subjected to a partial reduction roast to reduce the Fe(III) back to Fe(II) without reducing the Ti(IV) to Ti(III). The influence of reduction was studied by varying the reduction time between 5 and 80 min. Table 41 gives the phase-chemical composition of the slag after oxidation, reduction and leaching.

Table 41. The phase-chemical composition, as determined by XRD, of standard slag after oxidation, reduction and leaching. The samples are categorised by the retention time during reduction. The slag was oxidised at 850 °C for 2 h in 8% O₂, and reduced in 100 % CO.

Phase composition after oxidation		Major phase	Minor phase	Trace phase
Sample	PFE			
Feed	986	Rutile	FeTi-Oxide	Anatase
Phase composition after reduction		Major phase	Minor phase	Trace phase
Sample	PFE			
5 min	1439	Rutile	FeTi-Oxide; Anatase	Ilmenite
10 min	1475	Rutile	FeTi-Oxide; Anatase	Ilmenite
20 min	1356	Rutile	FeTi-Oxide; Anatase	Ilmenite
40 min	1481	Rutile	FeTi-Oxide; Anatase	Ilmenite; Iron
80 min	1487	Rutile	FeTi-Oxide; Anatase	Iron; Ilmenite
Phase composition after leaching		Major phase	Minor phase	Trace phase
Sample	PFE			
5 min	1444	Anatase; Rutile		FeTi-Oxide
10 min	1480	Anatase; Rutile		FeTi-Oxide
20 min	1361	Rutile	Anatase	FeTi-Oxide
40 min	1486	Rutile; Anatase		FeTi-Oxide
80 min	1492	Rutile	Anatase	

Legend: FeTi-Oxide – M₃O₅ solid solution; Rutile – TiO₂; Anatase – TiO₂; Ilmenite – FeTiO₃; Iron – Fe⁰

Table 41 shows that ilmenite formed during reduction. Table 41 further shows that metallic iron formed when the reduction period is extended to 40 min. A reduction period of 80 min was not sufficient to reduce all of the iron to the metallic form. All the ilmenite is removed during leaching. The lowering of M₃O₅ to a trace component indicates that this phase is also partially removed during leaching. Anatase appears to be the dominant phase in the leach residues of samples reduced for 10 min or less, while rutile becomes the dominant phase in the leach residues of samples reduced for longer than 10 min. This might be related to the previously noted observation that TiO₂ initially forms as anatase during oxidation, but that it transforms to rutile as the duration of roasting is extended.

Figures 40 and 41 show the effect of reduction time on the final TiO₂ content of the slag and the % Fe extracted during leaching. The log sheets of the experiments are

given in Appendices IX to XIII. There appears to be no real difference in the final TiO_2 content of samples oxidised for 5 to 40 min, but the final TiO_2 content does decline if the reduction period is extended to 80 min. According to the leach curves the highest iron extraction was achieved after a reduction period of 20 min. It is also interesting to note that leach behaviour changes when the slag is reduced for 80 min. When the slag is reduced for shorter periods the initial leach rate is very high, but it declines sharply after 2 h. In contrast the initial leach rate of slag reduced for 80 min is lower, but the decline in rate after 2 h is much more gradual.

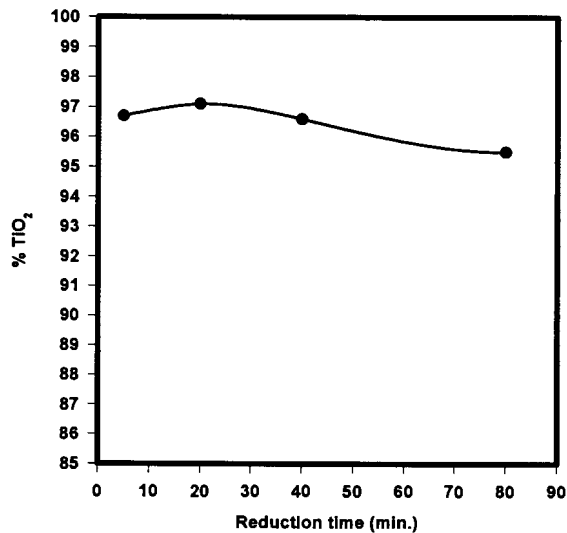


Figure 40. The influence of reduction time, during roasting of standard slag, on BTS product grade. The slag was oxidised for 2 h at 850 °C in 8 % O_2 , reduced in 100 % CO and leached for 12 h in boiling 20 % HCl.

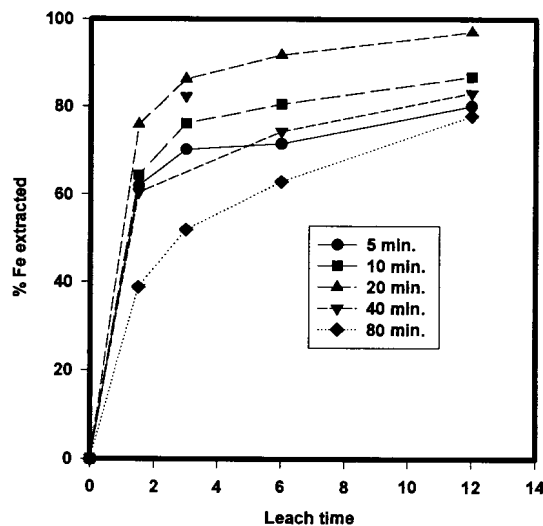


Figure 41. The influence of reduction time during roasting of standard slag on the rate of iron extraction during leaching. The slag was oxidised for 2 h at 850 °C in 8 % O_2 , reduced in 100 % CO and leached for 12 h in boiling 20 % HCl.

To quantify the phase changes that occur during reduction a Mössbauer investigation was conducted (See Appendix XVIII for the detailed results). The phase chemical compositions of the samples submitted for analysis are presented in Table 42. The samples were all oxidised for 2 h at 850°C in 10 % O₂ before they were reduced in 100 % CO for various times. The results presented in Table 42 are similar to the reduction results presented in Table 41.

Table 42. Phase chemical composition, as determined by XRD, of the oxidised and reduced samples submitted for Mössbauer analysis.

Reduced for:	PFE	Mineralogical composition		
		Main	Minor	Trace
5 min	3068	Rutile, Anatase	FeTi-Oxide	Ilmenite
10 min	3069	Rutile	Anatase, FeTi-Oxide	Ilmenite
20 min	3070	Rutile	Anatase, FeTi-Oxide	Ilmenite, Iron

Legend: FeTi-Oxide – M₃O₅ solid solution; Rutile – TiO₂; Anatase – TiO₂; Ilmenite – FeTiO₃; Iron – Fe⁰

The changes in the oxidation state of iron during reduction are presented in Figure 42. This shows that all of the Fe(III) has been reduced to either Fe(II) or Fe⁰ after 20 min. Metallic iron started to appear after 10 min of reduction. Figure 43 shows the changes in the abundance of the iron containing phases relative to each other. The Fe₂TiO₅ component of the M₃O₅ solid solution and the hematite component of the M₂O₃ solid solution decline rapidly and are converted to FeTi₂O₅ and ilmenite. With extended roasting times metallic iron starts to appear.

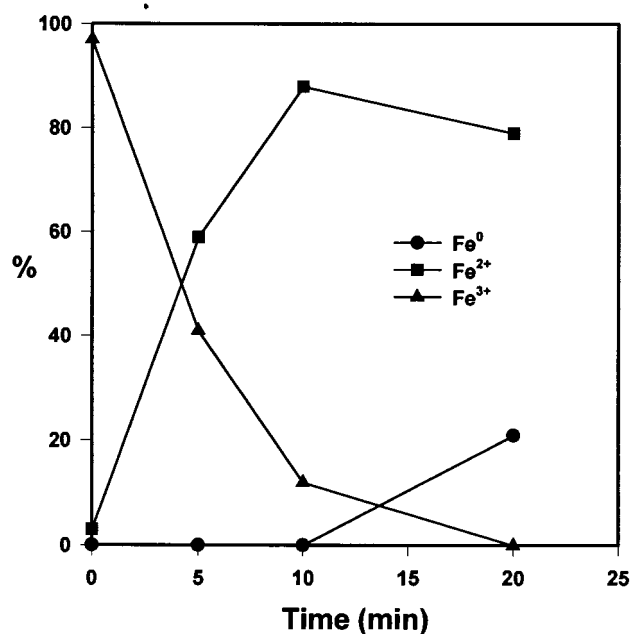


Figure 42. The changes in the oxidation state of iron during reduction as determined by Mössbauer analysis.

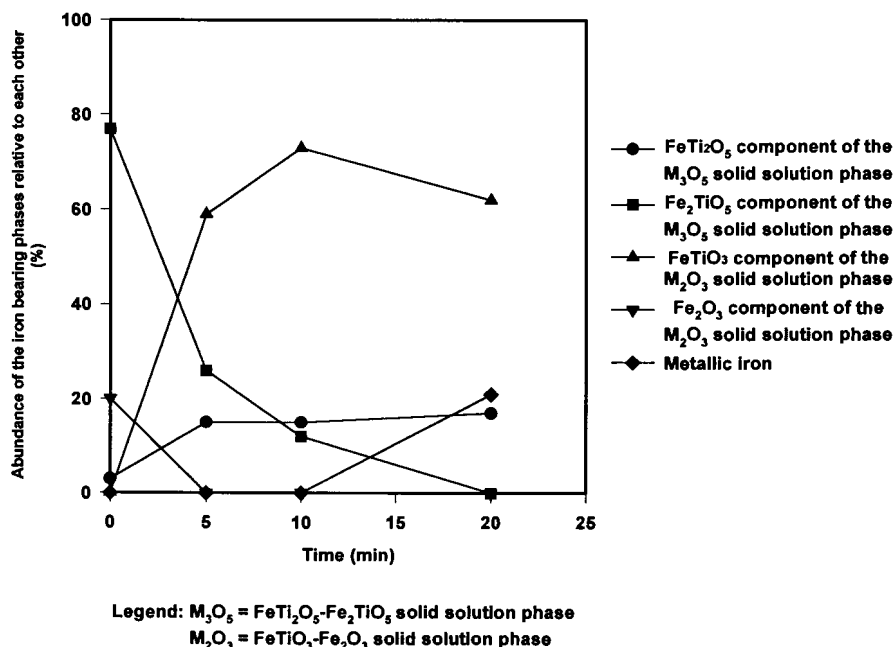


Figure 43. The changes in the relative concentration of the iron containing phases in oxidised standard titania slag during reduction for various times as determined by Mössbauer analysis.

4.3.1.3 Particle size

The influence of particle size was studied by subjecting three different size fractions, +150-300 μm , +300-500 μm and +500-700 μm , to the same oxidation, reduction and leach procedure. Table 43 gives the phase-chemical composition of the various size fractions after the various processing stages.

Table 43. The phase-chemical composition, as determined by XRD, of standard slag after oxidation, reduction and leaching. The samples are categorised by the size distribution used. The slag was oxidised at 850 °C for 2 h in 8 % O₂, reduced in 100 % CO for 20 min and leached in boiling 20 % HCl for 12 h.

Phase composition after oxidation		Major phases	Minor phases	Trace phases
Sample	PFE			
+150-300 μm	1374	Rutile	FeTi-Oxide; Anatase	-
+300-500 μm	1375	Rutile	FeTi-Oxide; Anatase	-
+500-700 μm	1376	Rutile	-	FeTi-Oxide; Anatase
Phase composition after reduction		Major phases	Minor phases	Trace phases
Sample	PFE			
+150-300 μm	1350	Rutile	FeTi-Oxide	Ilmenite; Anatase
+300-500 μm	1356	Rutile	FeTi-Oxide	Ilmenite; Anatase
+500-700 μm	1385	Rutile	-	FeTi-Oxide; Ilmenite; Anatase
Phase composition after leaching		Major phases	Minor phases	Trace phases
Sample	PFE			
+150-300 μm	1355	Rutile	-	Anatase; FeTi-Oxide
+300-500 μm	1361	Rutile	Anatase	FeTi-Oxide
+500-700 μm	1390	Rutile	-	Anatase; FeTi-Oxide

Legend: FeTi-Oxide – M₃O₅ solid solution; Rutile – TiO₂; Anatase – TiO₂; Ilmenite – FeTiO₃; Iron – Fe⁰

Table 43 shows that the slag samples contain mostly rutile after oxidation, but that the relative amount of rutile is much larger in the coarser size fraction. This larger amount of rutile in the coarser size fraction might be a result of the presence of primary rutile crystals from the smelting stage. Ilmenite formed during reduction. The ilmenite phase was removed during leaching and the relative amount of M_3O_5 in the slag also declined as a result of leaching. Figures 44, 45 and 46 show the effect of particle size on the final TiO_2 content and the iron extraction during leaching.

Figures 44 and 45 show that iron extraction and final TiO_2 content increase with decreasing particle size, but there is a much smaller difference between the iron extraction and the final TiO_2 content of the +150-300 μm fraction and the +300-500 μm fraction compared to the +500-700 μm fraction. Figure 46 shows that an increase in the oxidation time does not have a big influence on the amount of iron extracted from the fine +150+300 μm size fraction, the amount of iron extracted increases drastically for the coarser size fractions when the oxidation time is increased. This can probably be explained by the observation that the relative rate of oxidation increases as the particle size of the slag decreases (based on the observed shrinking core behaviour). As a result there are large unreacted cores present in the coarse particles that do not leach well.

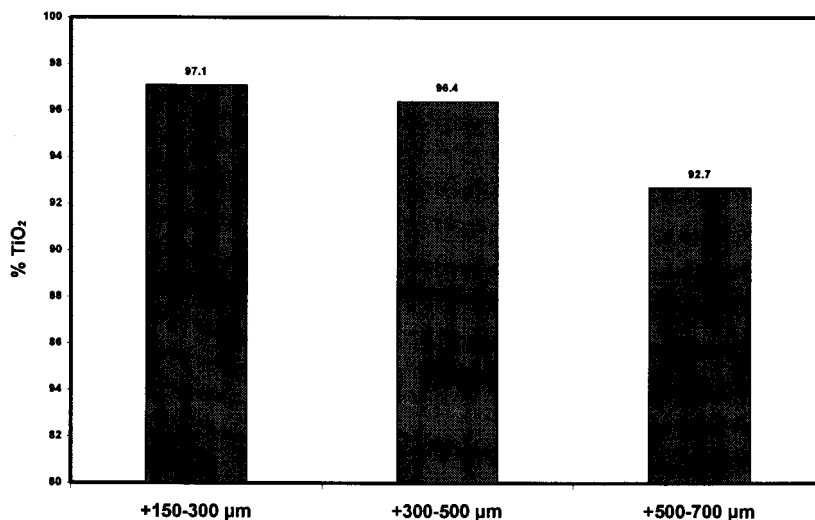


Figure 44. The influence of the particle size distribution of standard slag on BTS product grade. The slag was oxidised at 850 °C for 2 h in 8 % O_2 , reduced for 20 min in 100 % CO and leached for 12 h in 20 % HCl.

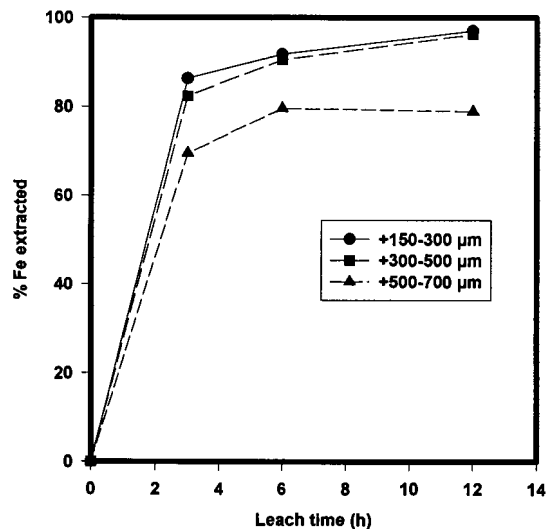


Figure 45. The influence of the particle size distribution of standard slag on iron extraction during leaching. The slag was oxidised at 850 °C for 2 h in 8 % O₂, reduced for 20 min in 100 % CO and leached for 12 h in boiling HCl.

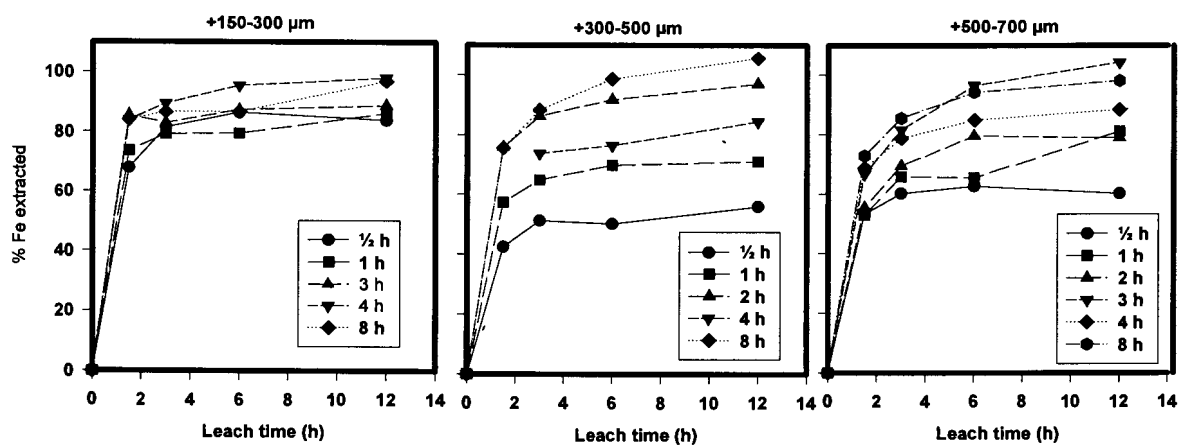


Figure 46. The influence of oxidation time and the particle size distribution of standard slag on the rate of iron extraction during leaching. The slag was oxidised at 850 °C in 8 % O₂, reduced for 20 min in 100 % CO and leached for 12 h in boiling 20 % HCl.

4.3.2 High iron titania slag

4.3.2.1 Oxidation

The effect of oxidation time

The high iron titania slag that was studied contained about 22 % FeO compared to the 9.3 % FeO in standard titania slag. The influence of oxidation on high iron slag was studied in a similar fashion to the standard slag by varying the duration of the

oxidation roast from 0.5 to 8 h. Table 44 gives the phase-chemical composition of the samples after oxidation.

Table 44. The phase-chemical composition of high iron titania slag after oxidation. The samples are categorised by the retention time during oxidation. The slag was oxidised at 850 °C in 8 % O₂

Phase composition		Major phase	Minor phase	Trace phase
Sample	PFE			
Feed	437	FeTi-Oxide	-	Ilmenite, Iron
Phase composition after oxidation		Major phase	Minor phase	Trace phase
Sample	PFE			
0.5 h	1167/1500	FeTi-Oxide	Rutile	Ilmenite; Anatase; Iron
1 h	1168/1501	FeTi-Oxide; Rutile	-	Anatase
2 h	1001/1502	FeTi-Oxide; Rutile	-	Anatase; Ilmenite
3 h	-	-	-	-
4 h	1169/1504	FeTi-Oxide; Rutile	Anatase	-
8 h	1505	FeTi-Oxide; Rutile	Anatase	-

Legend: FeTi-Oxide – M₃O₅ solid solution; Rutile – TiO₂; Anatase – TiO₂; Ilmenite – FeTiO₃; Iron – Fe⁰

Table 44 shows that the M₃O₅ phase transforms to rutile/anatase during oxidation. In contrast to the standard slag FeTi-Oxide remains as a major phase in the slag after oxidation. This is a result of the larger amount of iron in the slag. An optical and SEM investigation revealed that oxidation proceeded in a similar fashion to the standard slag. Samples which were oxidised for 0.5 h at 850 °C in 8 % O₂ (Figure 47), contained abundant partially reacted slag particles with a zoned appearance. There were - in contrast with the single iron-rim in the standard slag - two iron-rich rims in every particle, separated by a rutile-rich zone. The cores consisted primarily of the original M₃O₅-solid solution phase. The TiO₂-rich marginal zones appeared to be slightly porous and seemed to consist of a mixture of anatase and rutile. Rutile was present along cracks extending through the unreacted M₃O₅ particle cores. Finely disseminated metallic iron particles were also present in association with the rutile along cracks. The slag particles contained minor quantities of a silicate-rich glassy phase, usually situated at the grain boundaries of the individual titania crystals. The glass was characterised by the appearance of ilmenite crystallites as well as metallic iron. Disseminated, relatively coarse-grained metallic iron globules, associated with Fe-sulphide were present in the silicate-rich glass. Rounded “blebs” of a silicate-enriched glassy phase were also present embedded in the main glass phase.

The sample oxidised for 1 h at 850°C in 8% O₂ (Figure 48) appeared similar to samples that were oxidised for 0.5 h. The slag particles had a zoned texture with unreacted M₃O₅-rich cores and TiO₂-enriched, slightly porous marginal zones. The marginal zones might be slightly broader compared to the slag subjected to 0.5 hours oxidation. The fine-grained slag particles appeared to be more completely transformed to TiO₂.

The samples oxidised for 2 h at 850°C in 8% O₂ (Figure 49) appeared to be almost completely oxidised. Some coarser-grained slag particles with small unreacted M₃O₅-cores and broad TiO₂-rich outer margins were however still present.

The samples oxidised for 4 and 8 hours at 850°C in 8% O₂ (Figure 50) appeared to be completely oxidised (there were no unreacted cores). The marginal zones of the slag particles were characterised by the presence of rutile while the particle centres contained a mixture of sub-microscopic rutile and anatase. Some of the slag particles had dense anatase-rich centres.

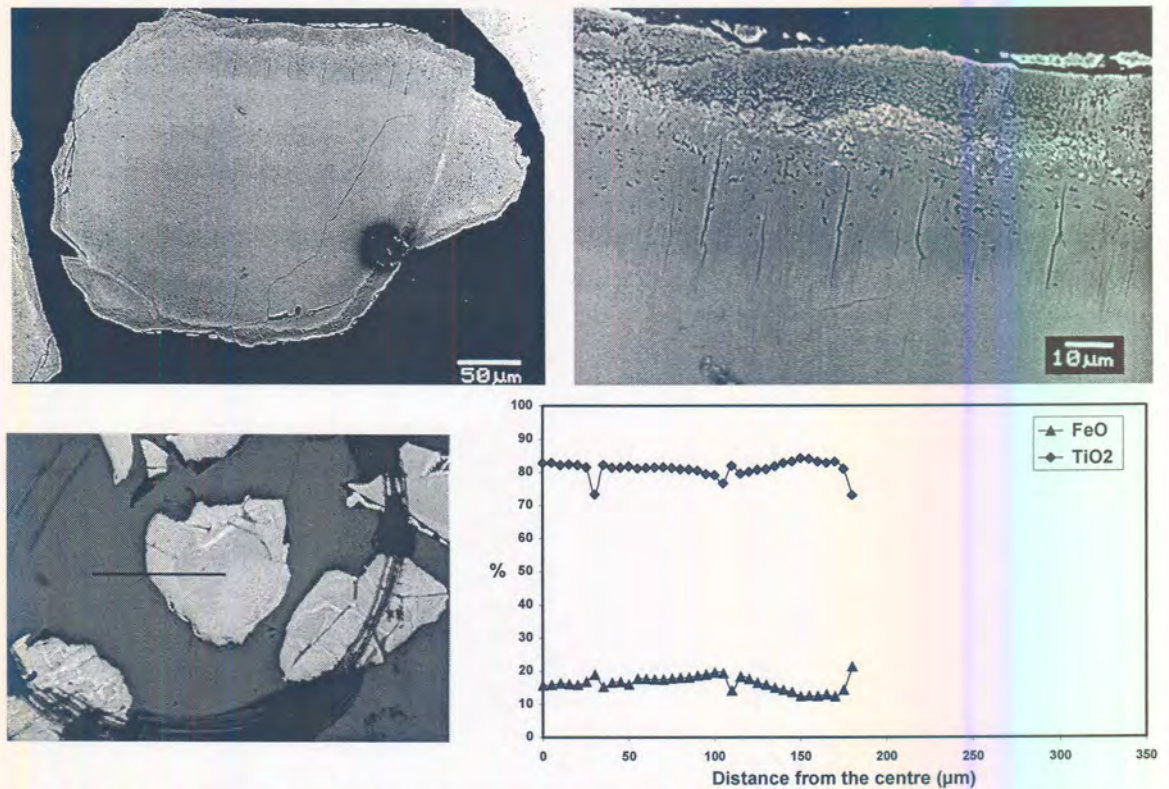


Figure 47. High iron titania slag oxidised for ½ h at 850 °C in 8 % O₂. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

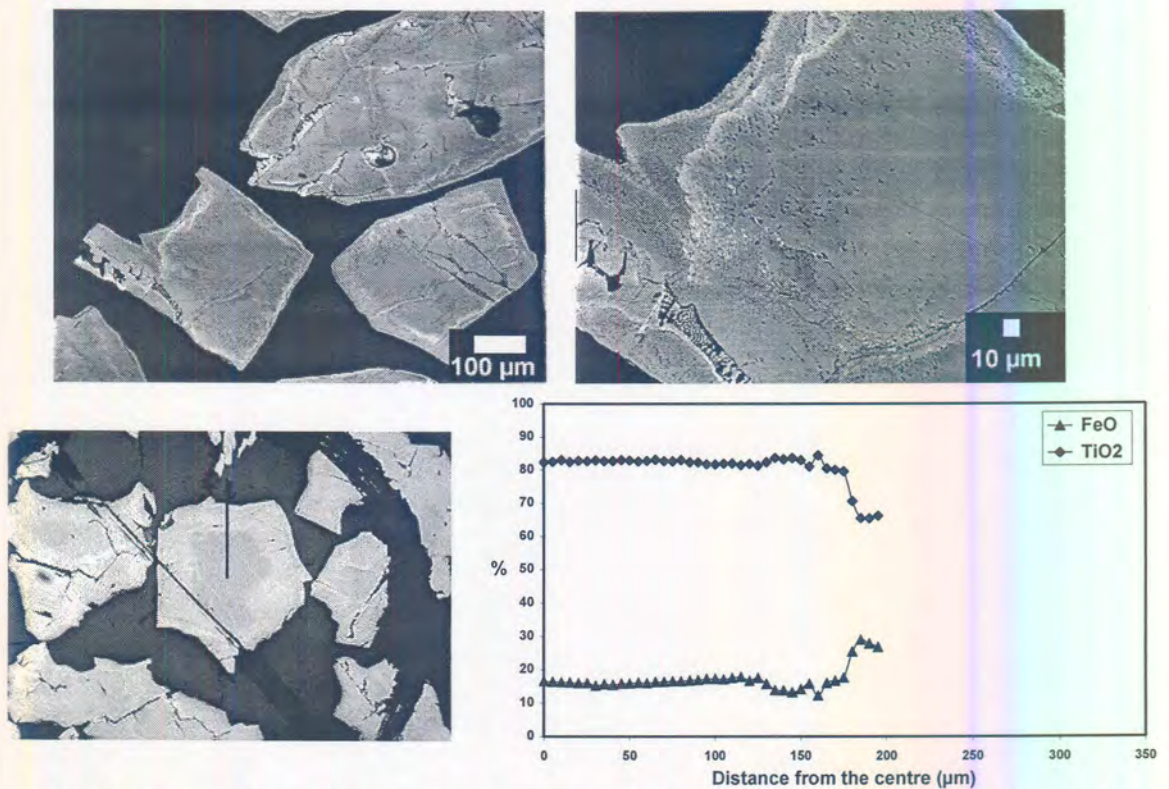


Figure 48. High iron titania slag oxidised for 1 h at 850 °C in 8 % O₂. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

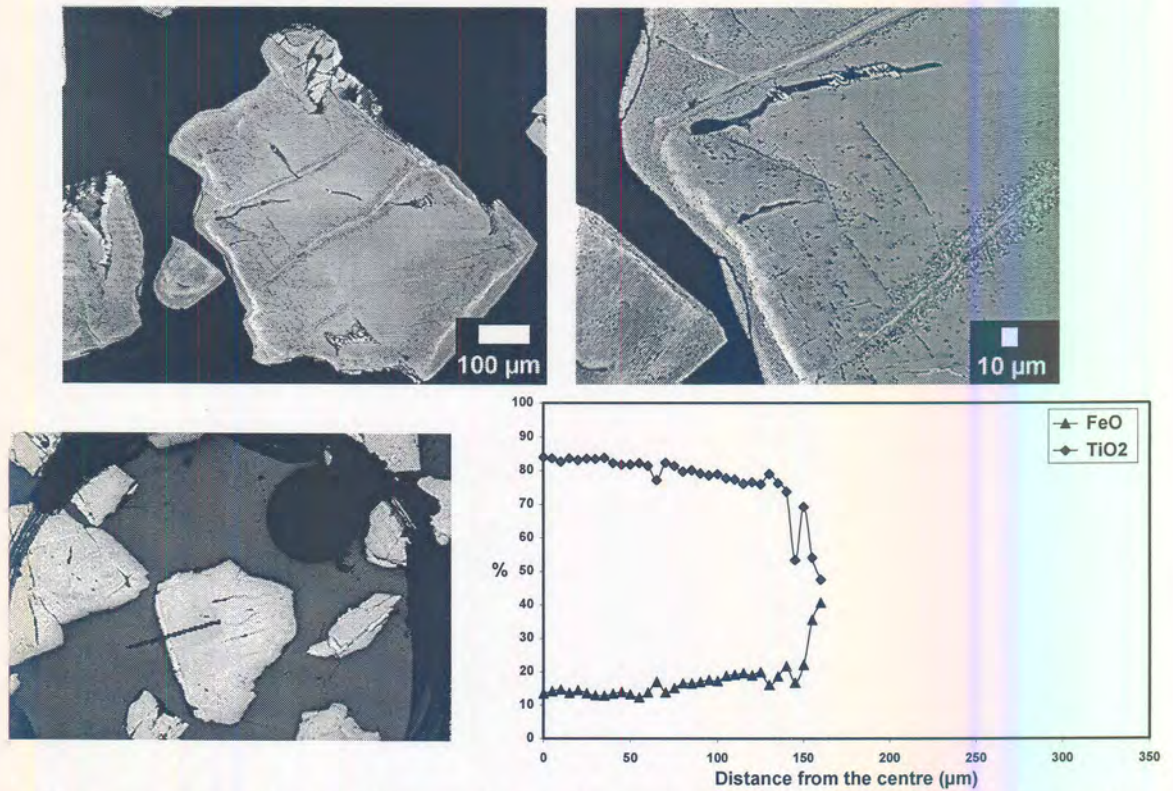


Figure 49. High iron titania slag oxidised for 2 h at 850 °C in 8 % O₂. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

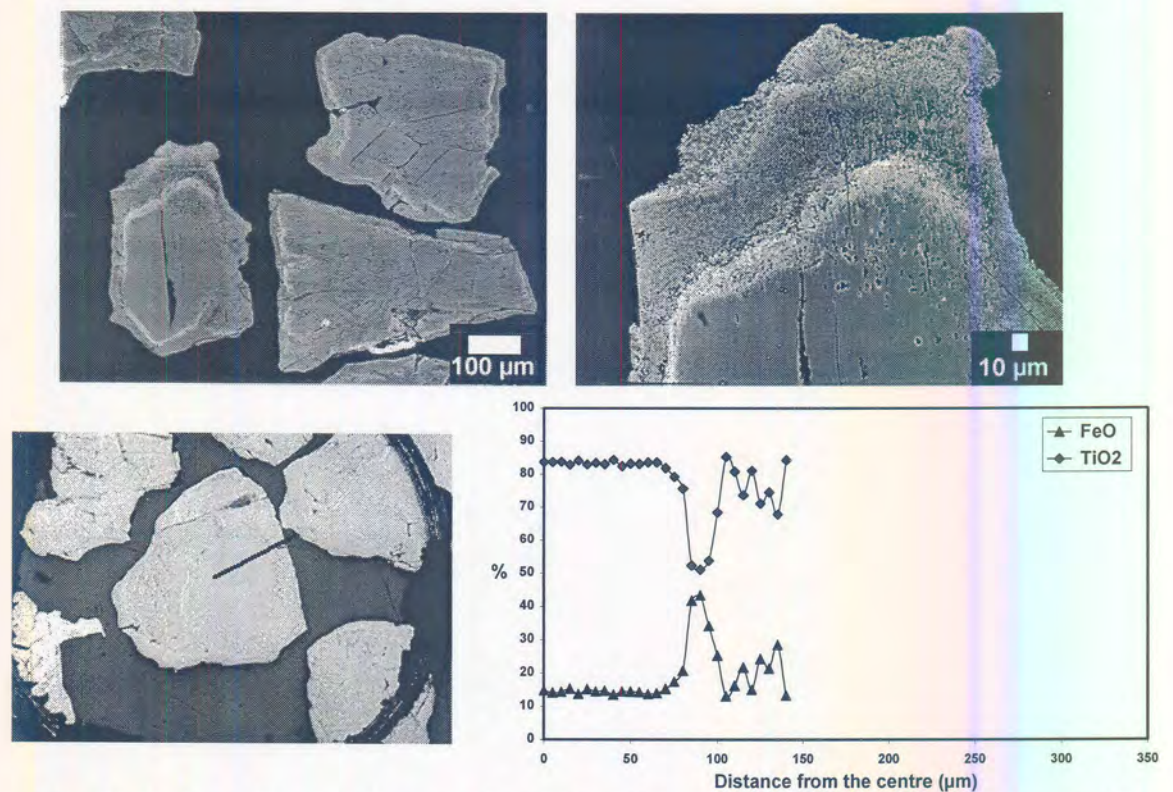


Figure 50. High iron titania slag oxidised for 4 h at 850 °C in 8 % O₂. SEM micrographs as well as a chemical composition profile (weight %) through one of the particles are shown.

Table 45. The phase-chemical composition of high iron titania slag after oxidation and reduction. The samples are categorised by the retention time during oxidation. The slag was oxidised at 850 °C in 8 % O₂ and reduced in 100 % CO for 20 min.

Phase composition after reduction		Major phase	Minor phase	Trace phase
Sample	PFE			
0.5 h	1197/ 1564	FeTi-Oxide; Rutile	Ilmenite	Anatase
1 h	1202/1606	Rutile; FeTi-Oxide	Ilmenite	Iron; Anatase
2 h	1109 /1612	Rutile	FeTi-Oxide; Ilmenite	Iron; Anatase
3 h	1618	Rutile	FeTi-Oxide; Ilmenite; Iron	Anatase
4 h	1207/ 1624	Rutile	FeTi-Oxide; Ilmenite	Anatase; Iron
8 h	1630	Rutile	FeTi-Oxide; Ilmenite	Iron; Anatase

Legend: FeTi-Oxide – M₃O₅ solid solution; Rutile – TiO₂; Anatase – TiO₂; Ilmenite – FeTiO₃; Iron – Fe⁰

Table 45 shows that ilmenite formed during reduction. Ilmenite is present in all the samples as a minor phase compared to the standard oxidised and reduced slag, where it occurred only as a trace component. The large amount of ilmenite in high iron slag may be as a result of the high iron content of the slag. The presence of M₃O₅ as a major phase in the samples oxidised for ½ h and 1 h indicates that these samples have not been completely oxidised. In the samples oxidised for 2 h or longer the M₃O₅ phase is only present as a minor phase after oxidation. This suggests that oxidation proceeded much further in these samples compared to the samples roasted for shorter periods. The optical and SEM investigation did not reveal any major morphological changes as a result of the reduction roast (Figure 51).

Table 46. The phase-chemical composition, as determined by XRD, of high iron slag after oxidation, reduction and leaching. The samples are categorised by the retention time during oxidation. For the experiments listed the slag was oxidised at 850°C in 8 % O₂, reduced for 20 min in 100 % CO and leached in 20 % HCl for 12 h.

Phase composition after leaching		Major phase	Minor phase	Trace phase
Sample	PFE			
0.5 h	1201/ 1569	Rutile	FeTi-Oxide	Anatase
1 h	1206 / 1611	Rutile	FeTi-Oxide	Anatase
2 h	1113 / 1617	Rutile;	FeTi-Oxide	Anatase
3 h	1623	Rutile	-	Anatase; FeTi-Oxide
4 h	1211/ 1629	Rutile	-	Anatase; FeTi-Oxide
8 h	1635	Rutile	-	Anatase; FeTi-Oxide

Legend: FeTi-Oxide – M₃O₅ solid solution; Rutile – TiO₂; Anatase – TiO₂; Ilmenite – FeTiO₃; Iron – Fe⁰

From Table 46 it appears that all of the ilmenite and a large amount of M₃O₅ are removed during leaching. In the samples oxidised for less than 2 h the M₃O₅ are present in minor amounts as a result of incomplete oxidation, while in samples oxidised for longer periods it is only present in trace quantities. The optical and SEM investigation revealed that structure of the slag changed from relatively dense to very porous during leaching. Only the outsides of the particles oxidised for periods up to 2 h were affected by leaching (Figure 52), while the particles oxidised for longer periods were leached more completely.

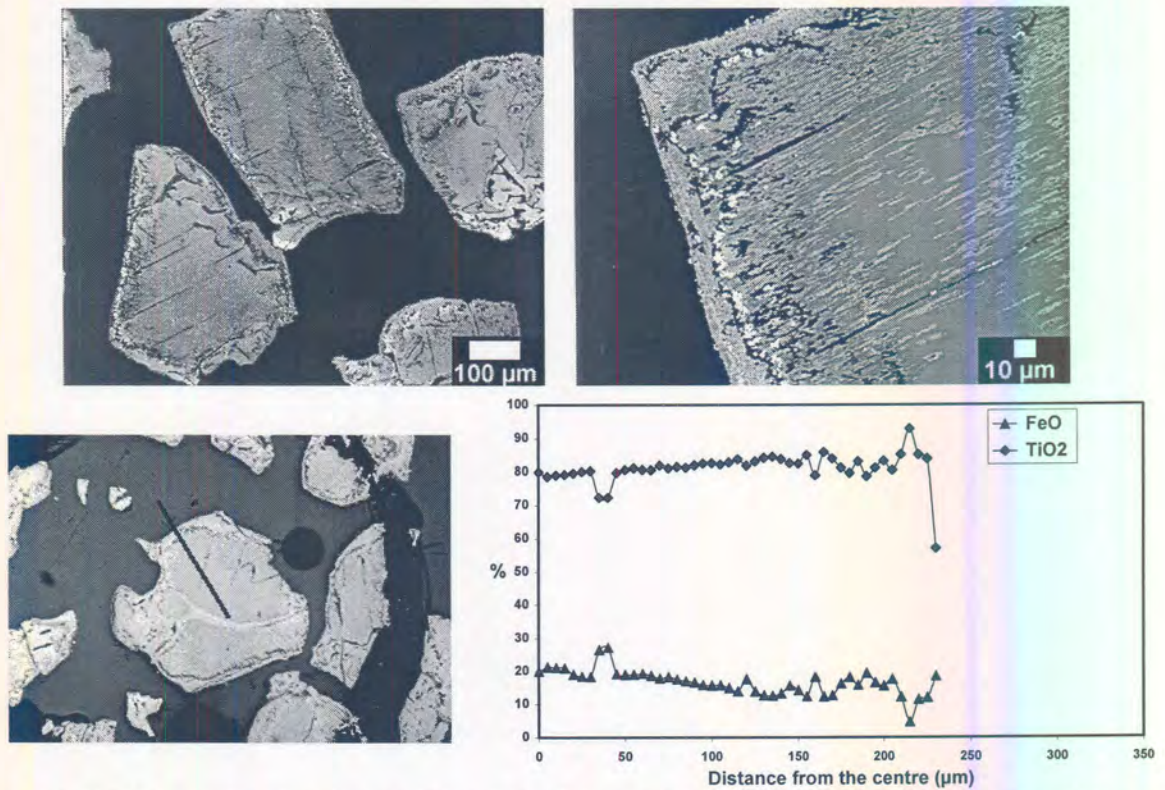


Figure 51. High iron titania slag oxidised for 2 h at 850 °C in 8 % O₂ and reduced for 20 min in 100 % CO. SEM micrographs as well as a chemical composition profile through one of the particles are shown.

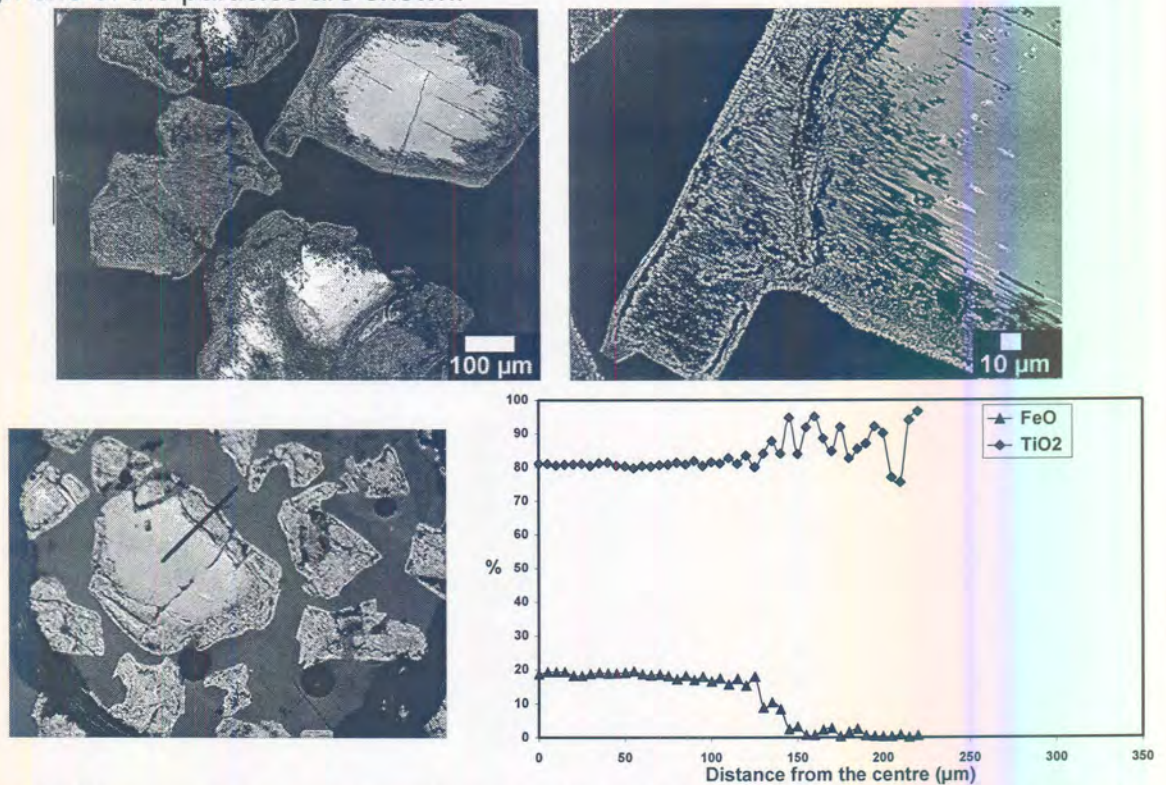


Figure 52. High iron titania slag oxidised for 4 h at 850 °C in 8 % O₂, reduced for 20 min in 100 % CO and leached for 12 h in boiling 20 % HCl. SEM micrographs as well as a chemical composition profile through one of the particles are shown.

The influence of oxidation time on the final TiO_2 content of the slag as well as the percentage of iron extracted during leaching are shown in Figures 53 and 54. The log sheets of the experiments are given in Appendices IX to XIII. The iron extraction for some of the experiments exceeded 100 % as a result of a poor accountability over these experiments. The poor accountability is due to the very small amount of slag available for leaching (5-10 g) after roasting samples were taken.

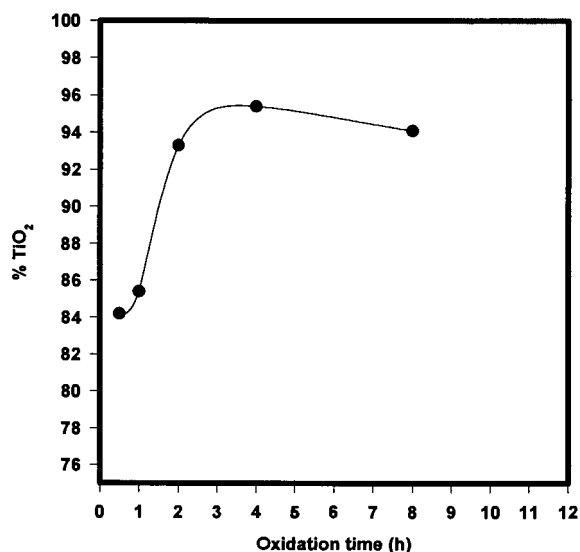


Figure 53. The influence of oxidation time, during roasting of high iron slag, on BTS product grade. The slag was oxidised at 850 °C in 8 % O_2 , reduced in 100 % CO for 20 min and leached for 12 h in boiling 20 % HCl.

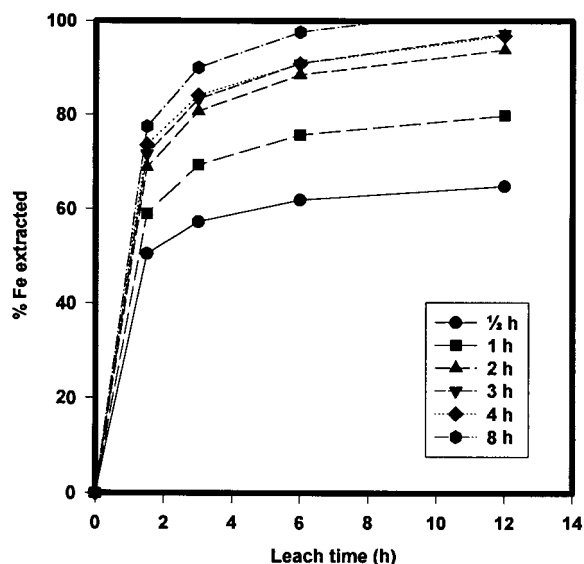


Figure 54. The influence of oxidation time, during roasting of high iron slag, on the rate of iron extraction during leaching. The slag was oxidised at 850 °C in 8 % O_2 , reduced in 100 % CO for 20 min and leached for 12 h in boiling 20 % HCl.

The final TiO_2 content of the slag increases as the oxidation time is increased up to 4 h. When the slag has been oxidised for 8 h there seems to be a slight decrease in the final TiO_2 content of the slag. The iron extraction follows a similar pattern to the final TiO_2 content and increases as the oxidation time increases, but in contrast to the final TiO_2 content there is no decrease as the oxidation time is extended to 8 h. This might be related to poor accountability of this particular experiment. As a result of a large liquid to solid ratio the concentration of metals in solution was very low. This introduced a large error on the liquor analyses. These results do suggest that the same mechanisms operate during the oxidation of high iron slag as during the oxidation of standard slag.

The effect of oxidation atmosphere and temperature

Oxidation is similarly influenced by the roasting temperature and the oxygen concentration of the oxidation atmosphere. The influence of the oxidation atmosphere was evaluated by varying the oxygen content of the fluidising gas, while the effect of roasting temperature was studied by varying it between 750 °C and 950 °C. The effects of oxidation atmosphere and roasting temperature on the final TiO_2 content and the iron extraction are shown in Figures 55 and 56. The log sheets of the experiments are given in Appendices IX to XIII.

The rate of oxidation in CO_2 is, as expected, very slow. This results in a final TiO_2 content below 85 % TiO_2 and a correspondingly low iron extraction. The final TiO_2 content and iron extraction increase dramatically when oxidation is conducted in air/ CO_2 gas mixtures. There does not appear to be an optimum oxygen concentration between 4 % and 21 % O_2 for the roasts conducted at 850 °C and 950 °C as there are no significant differences in the final TiO_2 content and the iron extraction when oxidation is conducted in these atmospheres. This is in contrast to the oxidation of standard slag where there appeared to be an optimum oxygen concentration for oxidation between 4 % and 8 % O_2 . The roasting temperature has a much more dramatic influence on oxidation compared to the effect of oxidation atmosphere. At 850°C and 950°C the final TiO_2 content is in the region of 90 %, but at 750 °C the maximum TiO_2 content is only 80 %. The iron extraction from the samples follows in general the pattern of the residual TiO_2 content, but once again there are some accountability problems that introduce some discrepancies. For example the high iron extraction in air at 750 °C is in contrast to the residual TiO_2 content of this experiment. Extractions in excess of 100 % were also calculated.

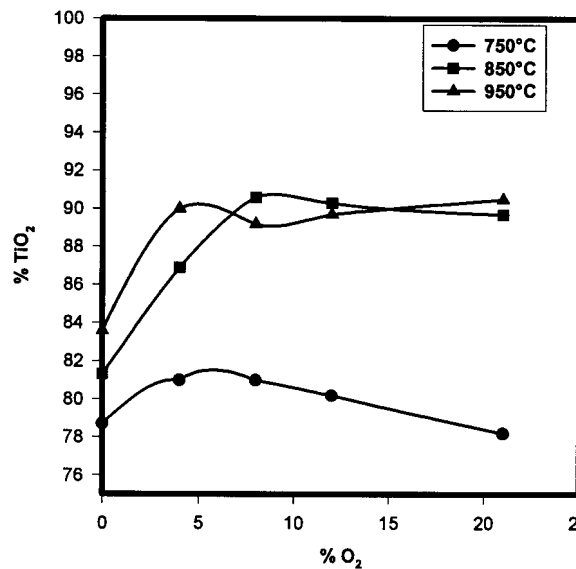


Figure 55. The influence of oxygen concentration and temperature (in air-CO₂ mixtures) during oxidation of high iron slag on BTS product grade. The slag was oxidised for 2 h, reduced for 20 min in 100% CO and leached for 12 h in boiling 20 % HCl. The slag contained and equivalent of 72% TiO₂ before treatment.

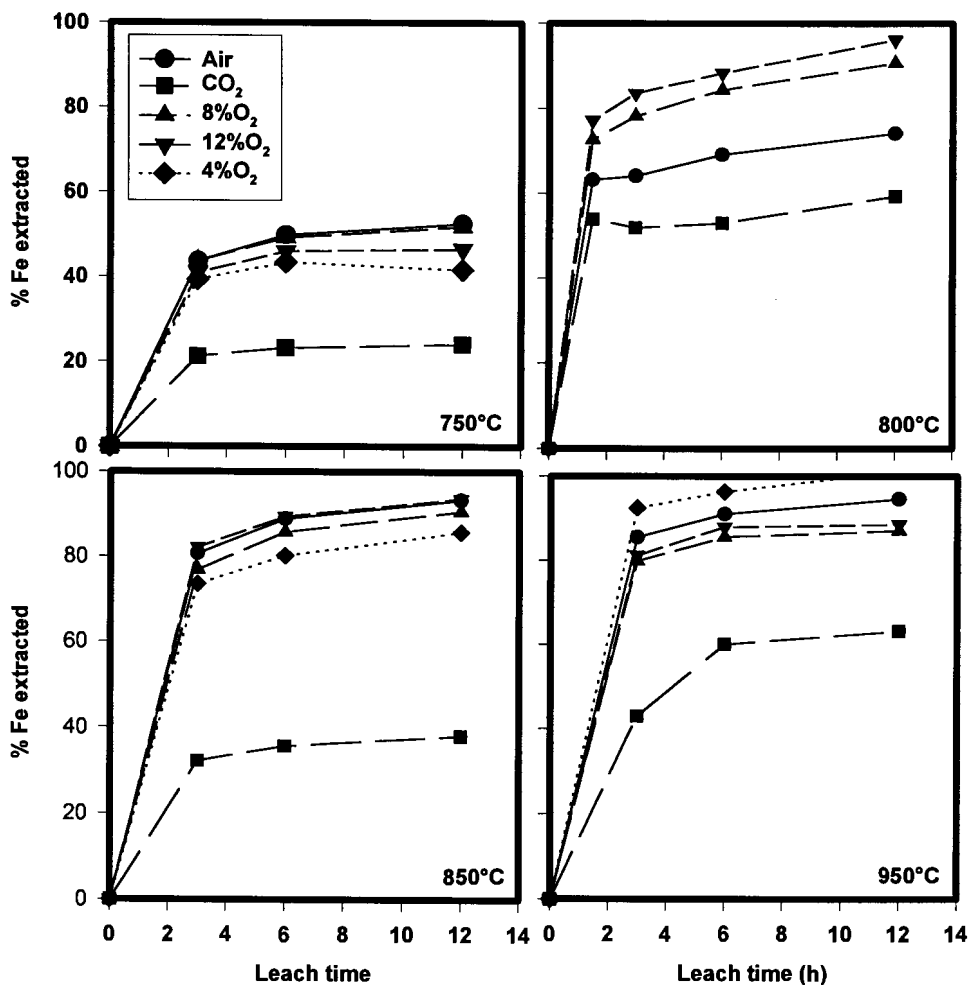


Figure 56. The influence of temperature and oxygen concentration during oxidation of high iron slag on the rate of iron extraction during leaching. The slag was oxidised for 2 h, reduced for 20 min in 100 % CO and leached for 12 h in 20 % HCl.

4.3.2.2 Particle size

The influence of particle size was studied by subjecting three different size fractions, +150-300 μm , +300-500 μm and +500-700 μm to the same oxidation, reduction and leach procedure. Figures 57 and 58 show the effect of particle size on the final TiO_2 content of the slag and the iron extraction during leaching. The final TiO_2 content of the slag increases as the particle size decreases. The difference between the final TiO_2 content of the finest and the coarsest size fractions is 8 % TiO_2 . These results suggest that the performance of high iron slag in the BTS process is highly dependent on the particle size distribution of the slag.

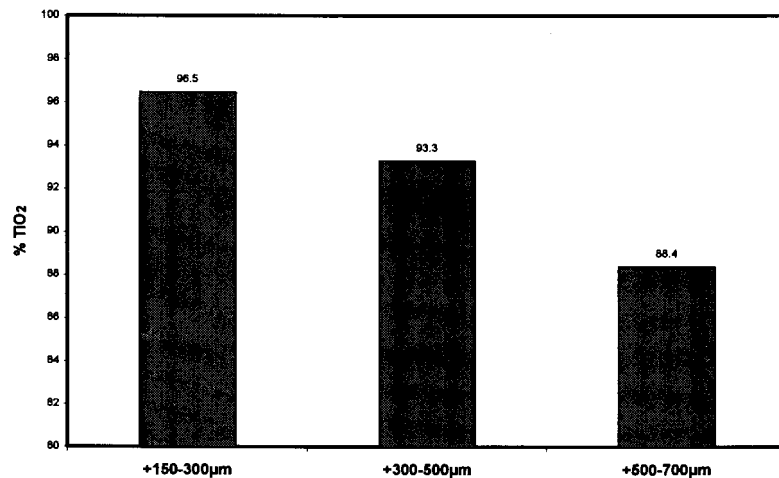


Figure 57. The effect of particle size distribution on final BTS grade. The slag was oxidised at 850°C for 2 h in 8% O_2 , reduced for 20 min in 100% CO and leached for 12 h in 20% HCl .

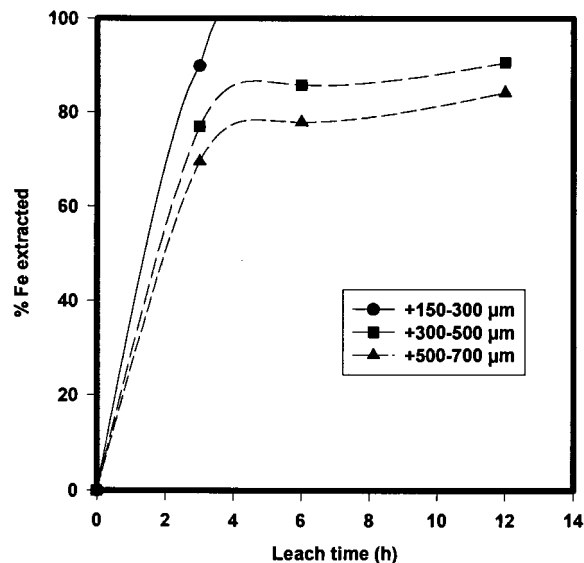


Figure 58. The influence of the particle size distribution of high iron slag on the rate of iron extraction during leaching. The slag was oxidised at 850°C for 2 h in 8% O_2 , reduced for 20 min in 100% CO and leached for 12 h in 20% HCl .

4.4 Conclusions

- Oxidation converts the original solid solution phase in the as-cast slag (M_3O_5) to TiO_2 and an iron-rich solid solution phase. This phase change is accompanied by the migration of iron to the outside rims of the particles.
- Reduction converts the iron-rich solid solution phase to ilmenite. The ilmenite is located on the particle rims in the areas of iron enrichment.
- The ilmenite phase is removed during leaching along with part of the iron-rich solid solution phase. This results in a beneficiated titania slag product.
- The optimum roasting conditions specified in Chapter 3 were oxidation at 850 °C for 3 h and reduction at 800 °C for 30 min. The best BTS grade produced in process development phase 1 was 94 % TiO_2 . Much better results were achieved during process development phase 2 and BTS with a TiO_2 content in excess of 97 % TiO_2 was produced. This may be related to the smaller sample sizes and the more controlled roasting conditions employed during process development phase 2. This allowed a good repeatability between experiments. The optimum process parameters were also refined through a large number of experiments.
- The oxidation rate (in terms of the relative amount of the M_3O_5 phase converted to TiO_2 and an iron-enriched rim) is lower for the higher-FeO slags.
- Two different roasting specifications can be drawn up from the results that have been presented. The conditions for producing a BTS product containing more than 95 % TiO_2 can be specified or the conditions for producing BTS with the highest possible TiO_2 content can be specified. In the following table these two specifications are listed for the materials that were investigated.

Standard titania slag	
Minimum specification	Maximum specification
<ul style="list-style-type: none"> • Oxidation: 1½ h at 850 °C in 8 % O_2 • Reduction: 10 min at 850 °C in 100 % CO 	<ul style="list-style-type: none"> • Oxidation: 3 h at 850 °C in 8 % O_2 • Reduction: 20 min at 850 °C in 100 % CO
Expected grade: 96.2 % TiO_2 1.52 % FeO	Expected grade: 97.5 % TiO_2 0.72 % FeO
High iron titania slag	
Minimum specification	Maximum specification
<ul style="list-style-type: none"> • Oxidation: 4 h at 850 °C in 8 % O_2 • Reduction: 20 min at 850 °C in 100 % CO 	Similar to the minimum specification
Expected grade: 95.4 % TiO_2 1.90 % FeO	