3. MINERALOGY OF WATER - GRANULATED HIGH - TITANIA SLAG.

As mentioned earlier water granulated titania slag was produced in a pilot smelter by fragmenting and rapid quenching of the liquid slag with a jet of cold water. On the other hand, block route slag was produced by collecting the liquid slag in a ladle and allowing the slag to cool down slowly for several days or weeks depending on the size of the blocks (Bessinger et al. 2001).

3.1 Analytical Techniques Used:

The instruments and techniques used during the whole project include the following:

X-ray Diffraction (XRD):

This technique was used to identify the crystalline phases present in the slag samples. Quantitatively, it was used to estimate the amounts of each phase in the slag samples. The samples were micronized in a micronizing mill with corundum and transferred into the standard Siemens sample holders. The powder was then pressed into the holder using a glass slide ready for the analysis to be carried out. A Siemens D-501 instrument was used with a copper (CuKα(1.5418Å)) radiation source and the analyses were carried out at 25^{O}C. The step width (2θ) and collection time per step were 0.040^{O} and 1.5s respectively. Table 3.1 shows the peaks and the values of 2θ used to quantify the relative peak heights of the different phases.

Table 3.1: The values of 2θ used to identify various phases.

Phases	**Angle (degree)**
Rutile	27.46
Anatase	62.53
Ilmenite	62.41
M_3O_5	18.12

Scanning Electron Microscope (SEM):

The samples for SEM analysis were prepared by mounting the slag particles in an epoxy based material, polished to obtain a smooth surface and coated with carbon or gold for electronic conductivity. Backscattered (BS) electrons were used for generating backscatter electron images in which phases and morphology of the polished surfaces cross sections were distinguished. The higher the average atomic number, the more electrons were backscattered thus the brighter the image.

Energy Dispersive Spectrometry (EDS) was used for qualitative and quantitative analysis. The elements were identified from peak positions and the peak intensities were related to the concentrations. A standard least squares method of quantification was applied where each element had an ideal spectrum in the system unto which the elements in the samples were compared.

The typical acceleration voltage 20kV and working distance of about 22.5mm were used .

Electron Probe Microanalysis (EPMA):

This analytical tool was used for microanalysis. The wavelengths of the characteristic X-rays, together with comprehensive sets of standards, were used to quantify compositions. The acceleration voltage of 15kV and a working distance of 11mm were used. This enabled us to determine the different oxidation states of both iron and titanium in the slag.

Mössbauer Spectroscopic analysis:

^{57}Fe Mössbauer - effect spectroscopy (MES) is a (nuclear) γ - radiation resonance technique involving the recoil-free emission radiation by the source and subsequent recoil – free absorption of this radiation by ^{57}Fe nuclei in the sample. This is a non-destructive analytical tool for establishing the oxidation state of iron (e.g. ferrous or ferric) and quantifying the different phases within the slag samples. The spectra parameters that serve as fingerprints during the analysis include isomer shift δ, quadrupole splitting Δ and internal magnetic field

(B_{hf}) all of which serve to characterize the chemical state of Fe in the slag sample.

The slag samples were powdered and MES measurements were conducted at room temperature using a 5-10mCi 57Co (Rh) radioactive Mössbauer source. Typically, 40-50mg/cm^2 of sample was used which correspond to 5-10mg/cm^2 of Fe. This was considered to be optimal thickness to ensure acceptable (i.e. at least 30%) transmission of the incident radiation. This was also to have adequate quantities of the ^{57}Fe isotope in the sample to ensure a satisfactory signal to noise ratio after 12-25 hours accumulation periods. For samples which show low iron content data accumulation was extended for 3-4 days to obtain an adequate signal to noise ratio necessary for a reliable analysis. Data analysis was effected by using the non-linear least square Mössbauer analysing programme (NORMOS). Final parameters of the fitted components were compared with accepted literature values for various iron-oxides and iron-titanium oxides to make a phase identification. These measurements were carried out by staff of the Department of Physics at the University of the Witwatersrand.

X-ray Fluorescence analysis (XRF):

The chemical method of analysis provided information on the average or bulk composition of the slag samples. Like in XRD, the samples were powdered and the analyses were carried out. The results were used to determine the mass balance of the entire chlorination process.

3.2. Experimental

The water-granulated slag sample C, and block route slag of the campaign (BSC) were provided by Kumba resources for chlorination in a fluidised bed reactor. A typical block route slag (BRS) was also provided. The granulated slag and block route slag of the campaign (BSC) were produced from the same ilmenite source. The purpose of block route slags was to serve as a control to establish the effect of water granulation on the chlorination behaviour of the slag. The block route slag (BSC) was fragmented mechanically to a size range of 425-

600μm before chlorination. On the other hand, the granulated slag sample was supplied as a mixture of different size ranges. The as-received granulated samples were separated into different fractions by using laboratory sieves with the following sizes; 106μm, 425μm, 600μm, 1180μm, 1700μm, 2360μm, 3350μm, and 4750μm. Both particles of size ranges 425μm -600μm and 1700μm -2360μm of granulated slag sample C were used in the chlorination experiments. The granulated slag of size 1700-2360μm and the block route slag (BRS) were crushed and sieved to the required particle sizes ready for chlorination. Samples of all size ranges were powdered in a tungsten carbide mill for qualitative XRD analysis to be carried out. The powdered samples were further micronized for quantitative determination of the different phases present in the samples. Finally the as-received samples of all size ranges were mounted in an epoxy based material and polished for SEM analysis to be carried out.

3.3 Results

The size distribution of the granulated slag samples (C) is given in figure 3.3.1. The results show quite a wide size distribution, with most of the particles being larger than the top size of 850μm generally required by chlorinators. The particles of the granulated slag in the size range 1700-2360μm were irregular in shape, figure 4.3b while the particles in the size range 425-600μm were both cylindrical and spherical, figure 4.3c.

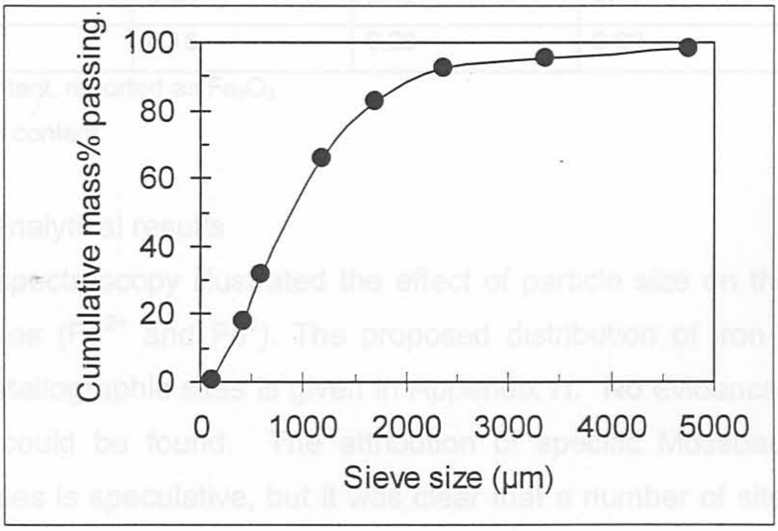

Figure 3.3.1: %Mass distribution of the particle sizes of granulated titania slag sample C.

X-Ray Floresence analytical results:

From the XRF analyses, the chemical composition of the block route slag (BRS), block route slag of the campaign (BSC) and granulated slag samples C are given in table 3.2 below, which reflects a slightly high iron content in the block route slags as compared to the granulated slag. The detailed XRF analyses for the three sets of samples are given in appendix K.

Table 3.2: % chemical composition of the two sets of samples used during the chlorination experiments as determined by XRF analysis.

Oxides	BSC	BRS	Granulated slag sample C
Al_2O_3	0.98	0.74	0.75
CaO	0.08	0.19	0.20
Cr_2O_3	0.11	0.20	0.07
$Fe_2O_3(t)^a$	13.62	16.99	11.22
MgO	1.02	1.47	1.06
MnO	1.53	1.13	1.21
SiO_2	1.04	1.21	1.28
$TiO_2(t)^b$	85.13	81.37	85.04
V_2O_5	0.44	0.45	0.46
Zr_2O	0.18	0.20	0.22

a Total iron content, reported as Fe_2O_3

b Total titanium content.

Mössbauer analytical results

Mössbauer spectroscopy illustrated the effect of particle size on the distribution of iron species (Fe^{2+} and Fe^0). The proposed distribution of iron between the different crystallographic sites is given in Appendix H. No evidence of any ferric (Fe^{3+}) ions could be found. The attribution of specific Mössbauer peaks to specific phases is speculative, but it was clear that a number of sites in addition to the ferrous pseudobrookite site were observed; these sites are variously labelled "ilmenite" and "sites A and B" in the Appendix H. However, these additional sites do indicate the presences of another iron-bearing phase in addition to the pseudobrookite. Solid solubility of a few percent of FeO in rutile has been reported, for the case where rutile formed by disproportionation of the M_3O_5 phase (oxidation of Ti^{3+} to Ti^{4+}, accompanied by reduction of FeO to Fe) (Teller et al. 1990). Hence it is suggested that at least some of the iron-filled sites detected by Mössbauer spectroscopy are in FeO-containing rutile.

XRD analytical results

The results generally showed that, four different phases, M_3O_5, rutile, anatase, and an "iron titanium oxide" were identified in the titania slags, figure 3.3.2. The relative amount of iron titanium oxide phase decreases as the particle size of the slag granules increases, appendix F. The "iron titanium oxide" phase is named as such in the XRD database; spectral information is available for this phase with the formula $Fe_{0.13}\,Ti_{0.81}\,O_{1.92}$ and shows a prominent peak at $2\theta = 28.74$. This is taken to be iron-containing rutile, which as mentioned above was also detected by MES.

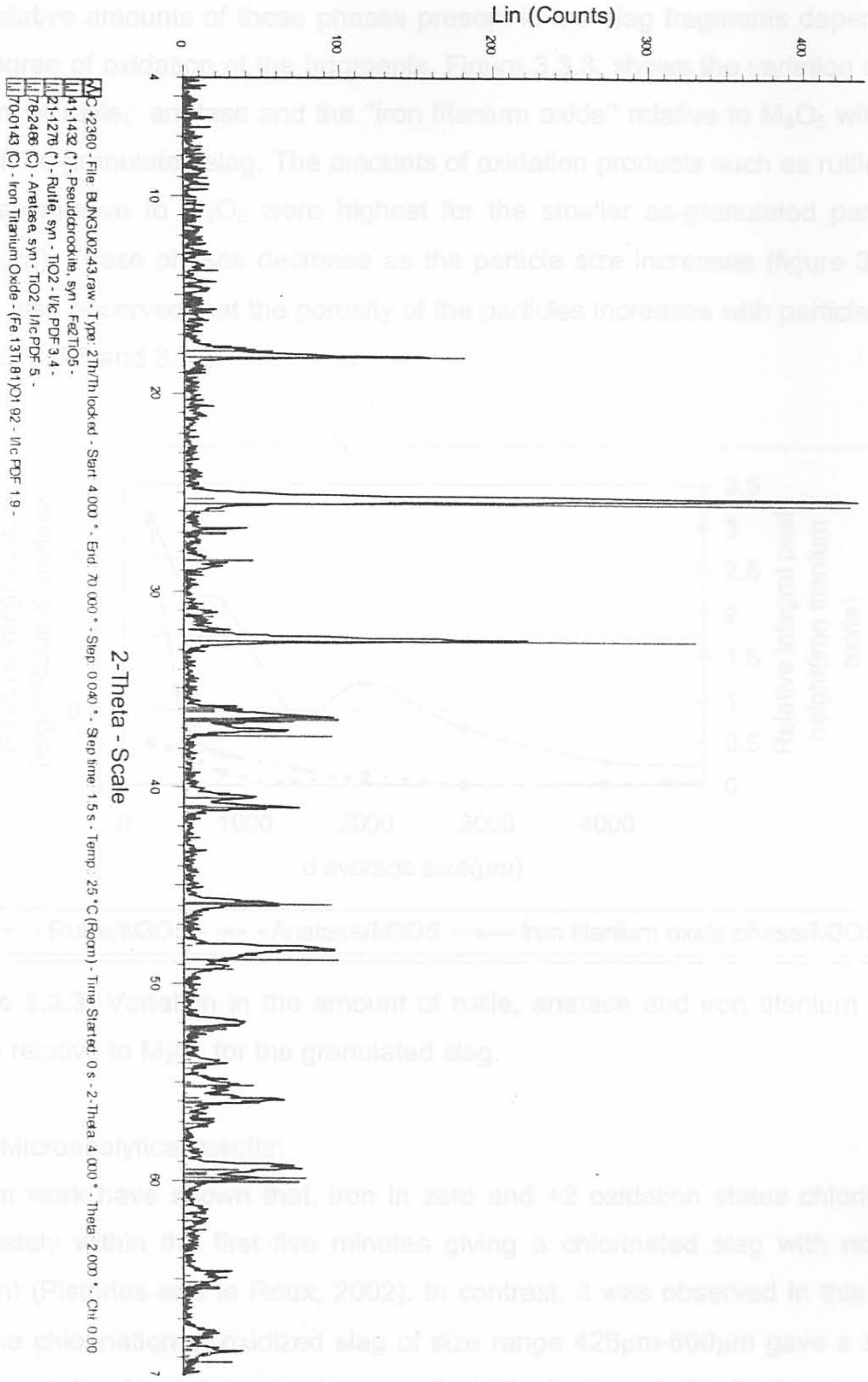

Figure 3.3.2: XRD spectrum showing four different phases present in oxidized titania slag of size range 2360 - 3350µm.

The relative amounts of these phases present in the slag fragments depend on the degree of oxidation of the fragments. Figure 3.3.3. shows the variation of the amount of rutile, anatase and the "iron titanium oxide" relative to M_3O_5 with the size of the granulated slag. The amounts of oxidation products such as rutile and anatase relative to M_3O_5 were highest for the smaller as-granulated particles (+106μm). These phases decrease as the particle size increases (figure 3.3.3). It was also observed that the porosity of the particles increases with particle size, Figures 3.3.5 and 3.3.6.

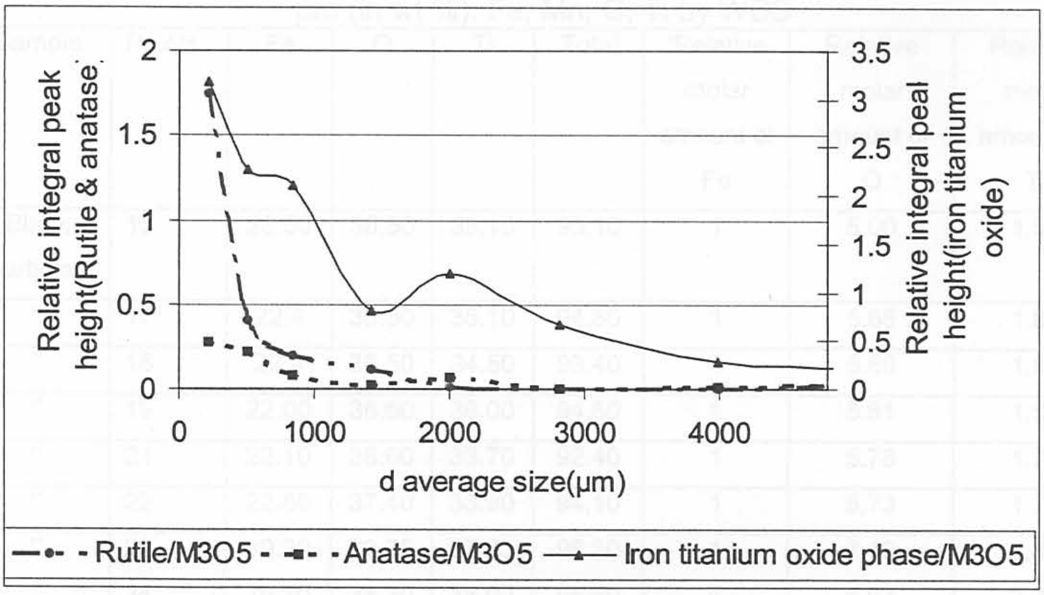

Figure 3.3.3: Variation in the amount of rutile, anatase and iron titanium oxide phase relative to M_3O_5 for the granulated slag.

WDS Microanalytical results:

Recent work have shown that, iron in zero and +2 oxidation states chlorinates completely within the first five minutes giving a chlorinated slag with no iron present (Pistorius and le Roux, 2002). In contrast, it was observed in this work that the chlorination of oxidized slag of size range 425μm-600μm gave a set of black particles (containing iron) even after 15 minutes of chlorination (as later shown in figure 4.4.3a and EDS analytical results, appendix E1). The off-white particles of the same size fractions and those of particles from the size range

1700µm-2360µm showed no iron present. The question was, in which oxidation state was the iron in these black particles? To provide answer to this question, the black particles were polished and sent for electron probe microanalysis where both WDS and EDS analysis were carried out.

Concentration in weight% of Fe, Mn, O, Ti and V were determined by WDS while the weight fraction of the other elements was determined by EDS. The full result is giving in appendix M while the result of the black particles is given in table 3.4

Table 3.4 Composition of chlorinated black particles of size range 425-600 µm (in wt %). Fe, Mn, O, Ti byWDS

Sample	Points	Fe	O	Ti	Total	‘Relative molar amount of Fe	Relative molar amount of O	Relative molar amount of Ti
Black particles	15	25.50	36.50	33.10	95.10	1	5.00	1.52
''	17	22.4	36.30	36.10	94.80	1	5.66	1.88
''	18	22.4	36.50	34.50	93.40	1	5.69	1.80
''	19	22.00	36.60	36.00	94.60	1	5.81	1.91
''	21	22.10	36.60	33.70	92.40	1	5.78	1.78
''	22	22.80	37.40	33.90	94.10	1	5.73	1.74
''	23	19.20	39.20	37.80	96.20	1	7.13	2.30
''	24	19.30	38.30	38.00	95.60	1	6.93	2.30
''	25	25.20	40.30	34.70	100.20	1	5.58	1.61
Average						1	5.92	1.87

Results in table 3.4 show that Fe, O, Ti in the black particles occur in the approximate ratio of 1:6:2 giving the empirical formula as $FeTi_2O_6$. This cannot be the true formula, since charge balance and the large oxygen content would require titanium to be present in an oxidation state higher than Ti^{4+} and/or iron in an oxidation state higher than Fe^{3+}. However, it appears that the WDS method slightly over-analysed oxygen and it was concluded that iron and titanium were most likely present in their highest oxidation states in this phase. Finally it was concluded that, the chlorinated slag particles in the smaller size range appeared black because they contain trivalent iron which could not be chlorinated, tetravalent titanium which chlorinates very slowly and magnesium oxide (See appendix M. The magnesium oxide chlorinates to form low vapour pressure or high boiling point liquid chlorides that tend to build up (Stanaway,1994).

SEM microanalysis.

Examination of the polished cross section slag samples using scanning electron microscope (SEM) with back-scattered electron imaging showed two main phases, appearing respectively higher-atomic number(Z) and lower-Z. Elemental analysis with energy dispersive spectroscopy (EDS) showed that the lower-Z regions were relatively titanium rich while the higher-Z regions were relatively iron rich, although with titanium remaining the main cation, see appendix A, B, C. Results for the smaller particles of size in the range 106-425µm, 425-600µm showed that oxidation had taken place throughout the particles, as the higher-Z and lower-Z regions were found randomly distributed throughout the particles. During this process, most of the Ti^{3+} in the M_3O_5 solid solution was converted to Ti^{4+} resulting in the precipitation of rutile and anatase as shown in the figure 3.3.4, hence confirming the previous results.

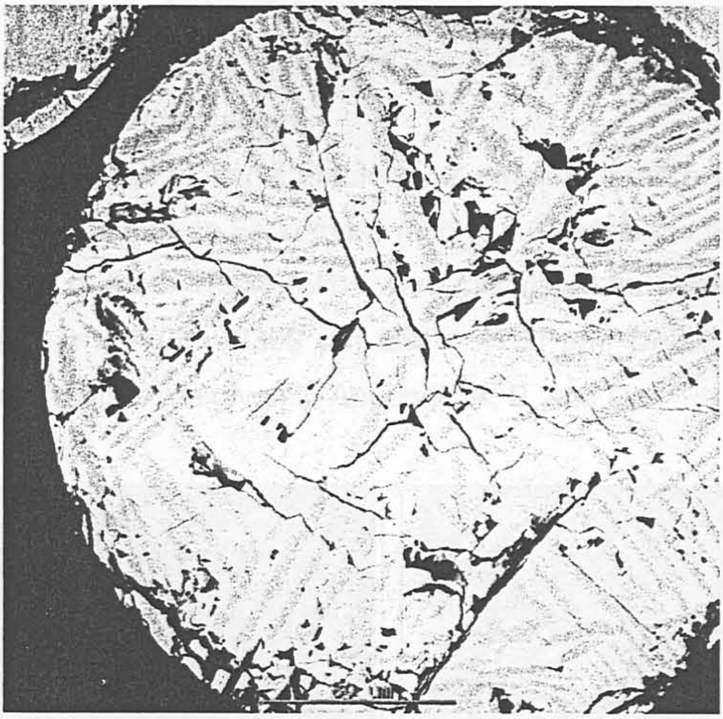

Fig 3.3.4; Granulated slag of size in the range 106-425μm showing random distribution of both lower-Z (iron-poor) and higher-Z (less iron-poor) phases throughout the particle. Back-scattered electron image.

Examination of the larger slag particles showed that, the relative extent (as a fraction of the total particle volume) of the oxidised (two-phased "higher-Z" and "lower-Z") regions decreases as the particle size of the granules increases, see for example figure 3.3.5a and b. These show the edge and centre part of the same particle in the size range of > 4750μm. The two-phased "higher-Z" and "lower-Z" regions are not randomly distributed throughout the particle but are more concentrated on the edge. This implied that the overall oxidation of the particles follows the topochemical reaction model. As stated earlier, the oxidized slags were found to be highly porous and the porosity increased with particle size. In contrast with this, the block route slag had a largely dense appearance, as can be seen in figure 3.3.6. The block route slag consisted primarily of M_3O_5 (pseudobrookite) phase. EDS analysis of uniform phase show an Fe/Ti ratio of 0.22 in addition to some impurities like Mg, Ca, Mn, and Al, see appendix D1.

Comparatively, XRF analysis of the same slag gave a percentage TiO_2 of 85.13% and Fe_2O_3 of 13.62% with Fe/Ti ratio of 0.16. These two results are comparable within experimental error.

EDS analysis of both the higher-Z and lower-Z phases of the oxidize slag show that the lower-Z phase had an Fe/Ti mass ratio of 0.03 while the higher-Z regions had an Fe/Ti ratio of 0.13. These ratios were calculated for particles in the size range 106 - 425 µm, 1700 - 2360 µm and > 4750 µm. Detail EDS analytical results for all size ranges are given in Appendix A, B, and C.

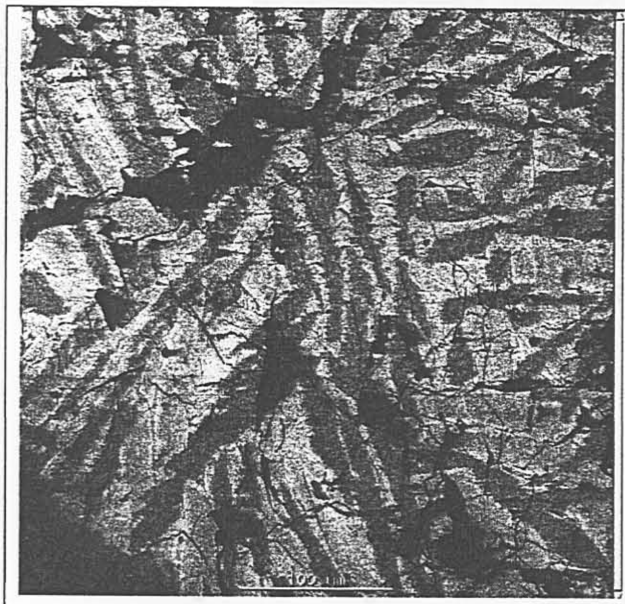

Fig. 3.3.5a; Edge of granulated slag of size range > 4750µm

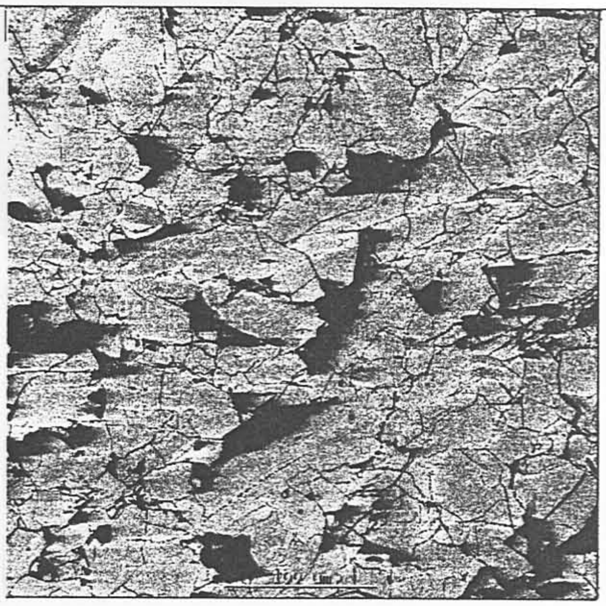

Fig. 3.3.5 b; Centre of granulated slag of size range > 4750µm

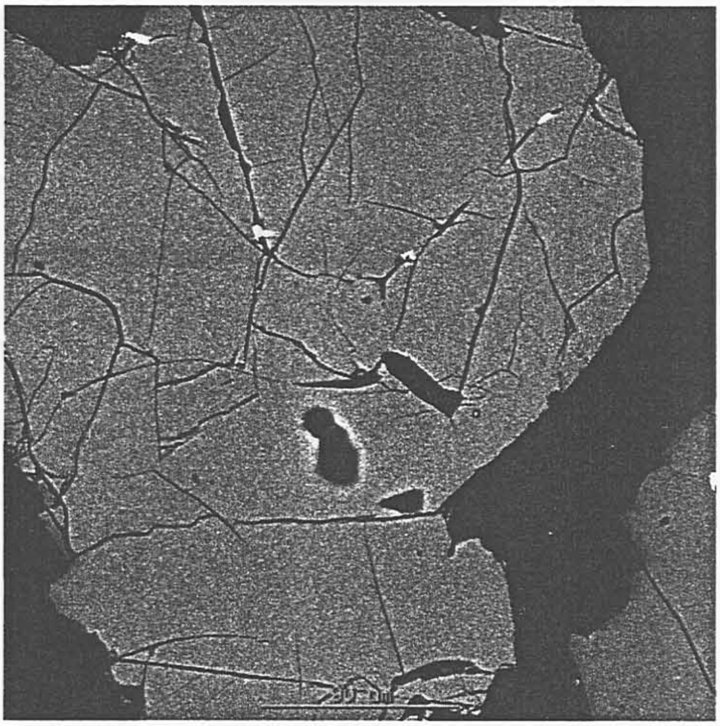

Fig. 3.3.6: SEM micrograph of block route slag of the campaign(BSC).

3.5 Conclusion:

Titania slag did undergo oxidation during water granulation, as a result, rutile (probably containing some FeO in solution for some particles) and iron-enriched pseudobrookite were formed as product phases. The nature of the black particles obtained after chlorination of the granulated slag in the size range 425-600µm showed that Fe^{2+} present in these particles did oxidise during granulation to Fe^{3+} as confirmed by WDS analysis. As mentioned earlier chlorination of this Fe^{3+} together with Ti^{4+} species in these particles is very slow, hence causing their non-porous nature. This might also be due to the presence of MgO which chlorinates to give high boiling point liquid. The association of the resultant chlorides and the slow reactive oxides account for the non-porosity of the slag. On the other hand, the second set of off–white particles obtained from the same batch of chlorinated sample and those of slag in the size range 1700-2360µm showed that these sets of particles contain mostly iron in the +2 oxidation state. The rapid initial chlorination of this Fe^{2+} species to form gaseous $FeCl_3$ created porosity in the particles hence accounting for their off–white and porous nature. The oxidation of the granulated slag was much more complete for smaller particles, and a reaction front at the particle edge was found for larger particles. From this, it appears that controlling the size of the granulated particles is a feasible method to control the average degree of oxidation of the granulated product.