Furnace dust from Exxaro Sands KZN

N. RUGHUBIR* and D. BESSINGER*
Research and Development, Exxaro

Exxaro Sands KZN produces—among other heavy mineral products—high titania slag, which is used as feedstock to the pigment industry. The titania slag is produced from the smelting of ilmenite in two 36 MW DC furnaces. In this smelting process carbon monoxide gas is produced. This gas is cooled, scrubbed and washed to remove entrained dust. This paper provides details on the gas cleaning plant system and the chemistry, mineralogy and size distribution of the particulate material contained in the off-gas stream. Characterization of the dust shows that it consists mainly of ilmenite, but with relatively high levels of SiO₂ and MnO. Smelting of the dust in a 500 kW DC furnace was carried out to investigate the potential for recovering valuable elements from the dust.

Introduction
Exxaro Sands KZN produces—among other heavy mineral products—high titania slag, which is used as feedstock to the pigment industry. Titania slag is the primary product from the ilmenite smelting process utilizing anthracite as reductant and electricity as the source of power. Exxaro Sands KZN is equipped with two 36 MW DC arc furnaces. The secondary product from the ilmenite smelting process is low manganese pig iron (LMPI), intended for consumption by the ductile iron market. The resulting carbon monoxide gas from the ilmenite smelting process passes through gas cleaning plants where the gas is cooled, scrubbed, and washed to remove entrained dust. The clean gas can be distributed throughout the site via a gas distribution plant or can be flared. The dust is slurried and then settled in a gravity separator (clarifier/thickener), returning clean water back to the plant water system. The dust is returned to the mine for rehabilitation back into the dunes. A history and general description of the plant has previously been given (Kotzé et al.).

This dust is currently considered a waste product with zero value. There is a strong probability that in future the cost of managing this waste stream will increase substantially. There, however, exists potential for unlocking some value from this dust. This paper investigates this by first looking at the chemical characteristics of the dust particles and then explores a potential smelting process for the recovery of the valuable constituents.

Furnace off-gas description
A schematic diagram of the furnace off-gas layout is given in Figure 1. The gas cleaning plant essentially consists of the following major components

- **Furnace off-gas duct**—the furnace off-gas duct transfers the hot and dusty CO gas from the furnace off-take (at approximately 1700°C) to the Theisen off-gas cleaning plant, which is designed as a disintegrator based wet scrubber plant. The furnace off-gas system consists of 5 segments, which are cooled indirectly by several cooling water circuits. The bottom section of the off-gas duct is spray cooled and is connected to the furnace gas off-take. The connection between gas off-take and off-gas duct allows for axial movement without risking gas leakage and external loads on the furnace roof. The same design is used at the connection to the evaporation cooler inlet flange.

- **Evaporation cooler ‘W20’**—the evaporation cooler vessel provides a reaction volume for the water to evaporate after injection into the CO gas transferred in the off-gas duct from the furnace. The shell of the vessel is cooled indirectly by two cooling water circuits. Due to the water, which is sprayed (temperature controlled) into the hot off-gas, the temperature of the furnace off-gas in the outlet of the evaporation cooler is reduced to approximately 500°C via injection water lances. The gas leaves the evaporation cooler either through the bottom outlet to the gas cleaning plant or via the top outlet to the emergency stack and the safety valve. Only one mode of operation is possible since both rotary hood water seals, B12 (shut-off valve in the flow direction of the emergency stack) and B13 (shut-off valve in the direction of the gas cleaning plant) are mutually interlocked.

- **Safety valve ‘B11’**—the safety valve limits the pressure in the furnace off-gas system by preventing air penetration into the gas system using a defined water level in the water seal of an immersion bell. If the system pressure increases above a defined value (i.e. due to material bridge collapse or eruptions in the furnace) the momentary gas surplus flows via the safety valve into the atmosphere. The immersion bell of the safety valve is set in such a way that gas flows immediately once the set value has been exceeded. On the other hand, in case of reduced pressure in the furnace, the water level drops only a little due to the large volume of water available in the tank. The resulting seal level between the bell and the interior duct prevents the penetration of air into the gas system.

- **Raw gas’ rotary hood water seal ‘B12’**—the ‘raw gas’ rotary hood water seal B12 regulates the raw gas path through the emergency stack ‘A12’. The rotary hood water seal operates as a quick-action valve with...
In the closed position, the hood is immersed on all sides in water, thus blocking off the flow of gas. The basic setting for the ‘raw gas’ rotary hood water seal B12 is the normally open position, but in any case of emergency the valve will be opened and the raw gas will leave the plant through the emergency stack. In closed position, compressed air is applied to the retracted cylinder for the ‘raw gas’ rotary hood water seal.

- **Ignition device ‘A 12/17’ for emergency/clean gas stack**—the raw/clean gas at the emergency/clean gas stack head is ignited by means of a separate ignition device using Sasol gas as fuel. The flame emerges at the chimney stack outlet and ignites the furnace gas.

- **Plant rotary hood water seal ‘B13’**—the plant rotary hood water seal ‘B13’ regulates the gas path through the gas cleaning plant. B13 is similar in design and operation to B12 described earlier. The basic setting for the B13 is the normally closed position this means the valve is open during normal plant operation, but in a case of emergency the valve will close and the raw gas will leave the plant through the emergency stack (B12 is then opened).

- **Cooling and washing tower ‘W14’**—gas cooling and coarse dust separation take place in the cooling and washing tower ‘W14’. The hot furnace gas is routed via the furnace off-gas duct and the evaporation cooler into the first stage of the cooling and washing tower where it is sprayed with water. This cools the gas and at the same time separates coarse dust. The coarse dust is carried with the water into the sump basin. Agitators are provided to avoid sludge deposits in the basin. The second stage of the cooling and washing tower serves the purpose of best possible precleaning and residual cooling to the required clean gas temperature. This is achieved by further spraying the gas with water by a special mushroom-shaped device in the cooling and wash tower. This device is adjustable so that the cooling and wash tower can be adapted to relevant operational requirements.

- **Theisen disintegrator gas washer ‘V15’**—the disintegrator gas washer ‘V15’ functions to separate the solid particles carried in the gas and compensates for the pressure losses in the gas system. The gas from the gas cooler enters the volute casing in an axial direction through the two inlet branches as in the case of a double-flow radial fan.

- **Water separator ‘F16’**—in the gas outlet of the disintegrator V15 there is a mixture of cleaned gas and the solid-loaded water which are separated from each other in the water, separator. The gas-water mixture enters the separator through the tangentially arranged inlet branch. Initial separation of the water droplets from the gas is achieved here by means of centrifugal forces. A mushroom-shaped insert in the separator further accelerates the gas-water mixture by way of its cross-sectional construction, similar to a Venturi tube, so that thorough separation of gas and liquid is achieved as the result of the inertia forces and centrifugal forces. The flow rate of the gas water mixture is reduced once again in the centre section of the centrifugal water separator where it is routed into the upper section of the centrifugal separator. The water droplets that were separated run downward along the wall and through the drain pipe into the circulation water basin. The gas, saturated with water vapour corresponding to the prevailing temperature, is now available as clean gas with the required residual dust content.

- **Off-gas slurry system**—the hot water from the furnace disintegrator discharges into a slurry sump (Theisen sumps). As the cooling water from the disintegrator contains a high concentration of solids, a mixer is used to ensure the solids do not settle out in the sump. Pumps are used to transfer the hot water (65°C) to the water plant discharging into the splitter box at the clarifier/thickener. From here the hot water can be
diverted to the clarifier/thicker. The clarifier/thickener is called a Multised (derived from ‘multiple seeding’). The Multised reduces the expected maximum concentration of suspended solids in the inflow down to less than 80 mg/l. The Multised performs the dual function of clarification and thickening, all in one unit. The Multised is fitted with lamella plates in the clarification section, thereby ensuring that exceptionally high rise rates can be maintained, while still producing water with a low turbidity. This results in the required construction area being substantially reduced, in comparison to conventional clarification/thickening equipment.

A picket-fence scraper underneath the clarification section allows sludge thickening in excess of 50% solids in the underflow. It must be noted that, although the Multised has a sludge thickening section, it is not a sludge blanket clarifier. Thickened sludge is discharged from the concentrate cone by a sludge waste pump to the sludge/slurry storage tank. Dust from the Fumex extraction plant (mainly metal treatment dust) is also transferred to the storage tank from where slurry tankers remove it and transport it to the mine for disposal on the residue dam. The amount of metal treatment dust is relatively small when compared to the amount of furnace dust generated. The clarified overflow from the Multised will flow under gravity to the off–gas hot well. The water is then circulated by the circulation pumps to packed cooling towers and discharges into the off gas cold well. From here the cooled water is transferred back to the furnace disintegrator via cold water recirculation pumps.

Characterization of furnace dust

The thickened sludge, also known as the thickener underflow, was sampled and characterized. Two samples were taken at the underflow position:

- Sample DB533—dust collected from the thickener underflow, in the form of slurry directly from the underflow valve
- Sample DB534—dust collected from the thickener underflow, in the form of wet solid that had accumulated on the floor below the underflow valve.

The samples were analysed by ICP. The forms of iron and titanium were determined by standard wet chemical techniques. Mineralogical (X-ray diffraction, optical and scanning electron microscopy) and size (Malvern mastersizer-ultrasonic sample dispersion) analyses were also carried out.

The chemical analyses of the two samples were similar, with Fe (21 to 25% Total Fe) and Ti (49 to 52% TiO₂) being the major components. The samples were enriched in Si (6 to 7% SiO₂), Mn (3.3 to 3.7% MnO), K (0.6 to 0.7% K₂O), Al (~1.15% Al₂O₃) and perhaps also Mg (1.1 to 1.3% MgO). This compares to values of 0.3% SiO₂, 1.1% MnO, 0.03% K₂O, 0.3% Al₂O₃ and 0.5% MgO typically found in the ilmenite. X-ray diffraction analyses of these samples indicate that ilmenite is the main phase present, with some rutile, metallic iron and the MnO₃ solid solution phases also present. Some carbonaceous particles were also identified (0.2% C present as per bulk chemical analyses for both samples). The X-ray diffraction pattern of sample DB533 is given in Figure 2.

The following phases were identified:
- Armalcolite - (Mg, Fe)Ti₃FeO₁₀ (M₃O₅ phase)
- Haematite - Fe₂O₃
- Ilmenite - FeTiO₃
- Metallic iron - Feº
- Magnetite - Fe₃O₄
- Quartz - SiO₂
- Rutile - TiO₂

The particles were identified as comprising the following phases:
- FeTi-oxides with the following variations:
  - FeTi-oxides resembling typical ilmenite compositions (dominant)
  - Rutile and Fe-rich rutile (subordinate)
  - FeTi-oxides with elevated Ti contents, resembling pseudobrookite and armalcolite-type compositions (occasionally).

The particles are mainly dense, but may also be porous, with the pores filled with silicates (mainly SiO₂, but sometimes also containing some K and Al). In addition, the porous particles are sometimes multi-phases containing various FeTi-oxide grains.

![Diffractogram of sample DB533](image)
Metallic iron (sometimes containing Ti) occurring as:
- Inclusions in the FeTi-oxides
- Interstitial in the porous FeTi-oxide particles
- Free-milling spherical particles (rare)

Haematite is also present as:
- Network of recrystallized laths or grains, cementing other grains
- As a rim around metallic Fe.

Others:
- Carbonaceous (reductant) particles
- Silicates (again, mainly SiO₂, but sometimes also containing K and Al)
- Fe-sulphide and Fe-sulphate as a rim surrounding metallic iron. The Fe-sulphate is probably an oxidation product from the Fe-sulphide, perhaps forming during the quenching and thickening of the slurry.

Of interest is the difference in the size distribution of the two samples, with the sample taken from the thickener underflow (sample DB533) being relatively coarse ($d_{50} = 189 \, \mu m$) while the sample taken off the floor below the valve (sample DB534) being fine ($d_{50} = 6.1 \, \mu m$). It is believed that the first sample might be from coarse material that had settled at the bottom of the tank and was obtained when the underflow valve was opened to take the sample. It might therefore not necessarily be a representative sample of the smelter dust. Despite this the chemistry and mineralogy of the two samples are similar. Particle size analyses of the two samples are shown in Figure 4.

For the first sample (Sample DB533) a clear bimodal distribution was observed. The first peak is situated at a particle diameter of between 0.1 and 1 \( \mu m \), while the maximum of the second peak is situated at approximately 300 \( \mu m \). For the second sample (sample DB534) there is one major peak, observed below 1 \( \mu m \). For this sample approximately 37% of the material is smaller than 1 \( \mu m \). It is again believed that the peaks situated below 1 \( \mu m \) are mainly due to fume condensates, whereas the larger particles are from the carry-over of particulate material into the off-gas system. No work was carried out to confirm the presence of fume condensates. It is, however, well known that elements such as silicon (fume as SiO) and manganese (fume as metal vapour) do present as fumes at high temperatures. If the -1 \( \mu m \) fraction is mainly due to fume condensate products (enriched in elements such as Si and Mn), the chemical quality of this dust might be improved by separating this fine material from the larger sized material.

**Smelting of dust in a 500 kW furnace**

A bulk furnace dust slurry sample was obtained for smelting tests. This sample was dried via electrically heated drying pans. During this drying process the fine dust agglomerated into a hard cake. This required some light milling to produce the required feed material used during the smelting tests. Approximately 3 t of dry furnace dust was obtained during this operation.

---

**Figure 3. Dust samples under microscope**

- Spherical FeTi-oxides (DB534)
- Original ilmenite grains (DB533)
- Various FeTi-oxides (DB534)
- Dense and porous FeTi-oxides (DB534)
- Fe-metal
- Fe-sulphide
- Fe-oxide
- Fe-sulphide
- Granular haematite
- Dense Fe-metal
- Ilmenite
- Porous
- Porous
- Ilmenite
- Pores
- FeTi-ox Porous
- Various FeTi-oxides (DB534)
- Occurrence of Fe-phases (bright) (DB534 and DB533)
The 500 kW furnace facility

The R&D pyrometallurgical facility contains a number of pilot-scale DC furnaces ranging from 200 kW to 1.5 MW units. It was decided to test the smelting of these materials in the 500 kW facility at R&D, situated in Pretoria West. The R&D team has gained extensive pyrometallurgical expertise during several ilmenite smelting campaigns prior to the construction of the 36 MW furnaces in Empangeni, KZN.

The 500 kW facility has a feed system comprising 4 hoppers mounted on load cell discharging into a single spirac feeder. The feed mix is discharged into the furnace via a feed port in the furnace roof. The power input is via 2 x 1.5 MVA transformers supplied from an 11 kV substation producing a maximum of 300 V/8kA DC from a 6-point rectifier to cathode. The furnace consists of a water-cooled cylindrical steel shell with magnesia refractory and a single central vertical electrode. The furnace has two tapholes.

Results from the smelting tests

The furnace was started with an initial scrap-metal burden. Gas preheating of the furnace was followed by arcing. Some reductant additions were made once the metal pool had been developed to increase the carbon content of the metal. The dust was fed into the furnace with the addition of reductant at different times, producing a slag of containing from 75–81% TiO₂ at a temperature of 1630–1670°C. Anthracite was used as reductant. The slag produced was of low TiO₂ quality, containing high SiO₂ and alkali components. Analysis of the slag obtained is shown in Table I, showing the high levels of contaminants. Also shown in Table I are some typical specifications for slag used in the downstream chloride process route for the production of pigments (Bessinger et al.).

Micrographs of a high silica slag are shown in Figure 5. The slag contained high SiO₂ levels, present mostly in glassy phases. These glassy phases contain many of the contaminants present. The glassy phases occur in the following ways (Figure 5):

- appearing to penetrate and partially dissolve the FeTi-oxide (A4)
- interstitial between the FeTi-oxide grains (A5)
- isolated and contained in the FeTi-oxide grains (A6).

Depending on the mineralogy of the slag, it may be possible to (after cooling) crush the slag and physically beneficiate it to get rid of the high SiO₂ fraction. These photos clearly illustrate how fine the glass phase particles are, requiring intensive milling to achieve liberation. An alternative would be to chemically treat the material to remove the contaminants in a hydrometallurgical process.

Conclusions

Smelter dust is currently returned to the mining site for disposal. This dust consists mainly of ilmenite, but with relatively high levels of SiO₂ and MnO. From the sieve analyses it seems that this dust consists of a fume condensate (< 1 μm) and particulate material from the furnace operation. Smelting of the dust produced a slag of low TiO₂ quality. High SiO₂ and alkali components can be identified as the main slag contaminants. Further treatment of the slag would be required to produce a marketable product. Technology to further treat the slag would need to be developed. The smelting cost, including the total preparation of pellets, smelting and slag treatment is expected to be substantial. The advantage of such a process...
is that some marketable products may be produced, which can generate revenue as opposed to returning dust back to the mine site. Saleable iron will also be produced from the smelting process, which will be an additional benefit. The treatment of the furnace dust will minimize the total site waste and has the potential of producing some saleable products.

References
