

The South African industry use of Mössbauer spectroscopy to solve operational problems

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Abstract South Africa is a country that is very rich in mineral resources but the use of Mössbauer spectroscopy to solve operational industrial problems is however very limited. In the Bushveld Igneous Complex the main minerals extracted from the ore are the platinum group metals and chromium, but secondary recovery of base metals such as nickel, copper and cobalt forms an integral part of the process. Losses of nickel in the slag can amount to about 4 % and subsequent a slag cleaning furnace is used to reduce the loss to less than 0.5 % nickel oxide. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and mineralogy was used to determine the partial oxygen pressure in the furnaces and also the efficiency of the nickel recovery. From the Mössbauer results, augmented with XRD, SEM, EMP-WDX and MLA analyses, optimum conditions were determined to ensure minimum metal losses. The use of Mössbauer spectroscopy in the coal industry, to investigate mineral changes that occur during its use, is also of importance. The main minerals present in coal were determined with the aid of various techniques, such as Mössbauer, XRD, SEM and HR-TEM, with the major iron minerals found to be pyrite, illite, ankerite and jarosite. A large quantity of coal is used to produce syngas via gasification plants for the production of synthetic fuels. The change of the mineral matter during gasification was studied and the changes occurring during the gasification process were followed. The syngas produced, is further treated by means of the Fischer–Tropsch process where an iron catalyst is incorporated in the process. The usefulness and fouling of the catalyst is being studied with the aid of Mössbauer spectroscopy. The calibration of equipment

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to determine work hardening in mining equipment was also investigated and found to be a useful tool in industry. From the above few examples it is evident that, although used on a limited base, Mössbauer spectroscopy, augmented by various other spectroscopic tools, still ensures optimal recovery and production of the vast resource base of South Africa.

Keywords Nickel · $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio · Coal · Syngas · Iron minerals · Mineral changes

1 Introduction

South Africa's total mineral reserves remain some of the world's most valuable, with an estimated worth of \$2.5-trillion, having the world's fifth-largest mining sector in terms of GDP value. It has the world's largest reserves of manganese and platinum group metals (PGMs) and among the largest reserves of gold, diamonds, chromite ore and vanadium [1]. Most of these reserves consist of ores that are complex in character and research is necessary before effective processes for their beneficiation can be put into operation. In the present paper various South African industry applications used over the years, are discussed.

Ferrosilicon (FeSi) forms the basis of the powder used in dense medium separation (DMS) in a minerals beneficiation process and is usually produced as angular (milled) or spheroid (atomised) particles [2] and stored in a lime solution, yielding a longer shelf life and minimum corrosive action to occur. Kumba Iron Ore Limited (owned by Anglo American) is a leading supplier of high quality iron ore to the global steel industry and uses the FeSi in the DMS operations to separate the iron ore from the gangue material. The FeSi is reclaimed from the process stream for re-use by means of magnetic separation [2]. Another use of FeSi is in the recovery of diamonds, by means of DMS, to reclaim the alluvial diamonds from the diamond-bearing gravels found along South Africa's West Coast [3]. The De Beers' Namaqualand Mines are situated along a 250 km stretch of the Atlantic coast of South Africa and mainly angular FeSi is being used in the DMS process. Current losses of FeSi, for example, in its DMS use in the iron ore recovery at Kumba Resources, Sishen, South Africa and the De Beers' Namaqualand Mines (now Trans Hex) occur due to adhesion to the separation products and also by being present in the effluent stream, due to abrasion [4]. The losses contribute greatly to the running cost of the plant and the purpose of this project was to determine the characteristics of the unused FeSi and then to characterise the changes that occur during storage and the use thereof.

Important heavy mineral bearing sands, containing ilmenite, rutile, zircon and monazite have been found in the North coast of Natal of South Africa. South Africa has about the 5th largest reserve of ilmenite, but mining takes place in a sensitive environmental area. A dredging process, to recover the ore reserve, is used and little is known about the applications of Mössbauer spectroscopy for the recovery of ilmenite from the mining and the mineral processing tailings [5]. Since the beach sand tailings, left after concentration of the valuable minerals, still contain some valuable minerals, a sequence of processes was developed to determine the optimum process to recover the ilmenite. The as-received beach sand tailings and the products from the screening-, flotation-, spiral concentrator and magnetic separation processes were monitored with room temperature ^{57}Fe -Mössbauer measurements.

In the mining industry, materials with a high abrasion resistance are needed, with white cast iron being an important material used as a liner for secondary mills and used in the beneficiation and production of the iron ore mentioned. High chromium white cast iron is an ideal material to be used after being heat-treated to retain the correct amount of austenite

phase. To achieve the correct wear resistance for a specific application does often not necessarily match with a high level of retained austenite phase in the material. The steel balls in a mill impact on the cast iron liners, resulting in work hardening and phase transformations to occur, followed by a volume expansion, which in turns cause the liners to expand and crack [6]. Thus the control of the retained austenite content may result in tuning the applications of this material. To measure the correct level of retained austenite, portable equipment using eddy current techniques, is needed to check each casting *in situ*. Calibration of this apparatus against laboratory methods such as XRD or CEMS was found to be viable and the apparatus can thus be used in the casting industry to ensure uniform casting manufacturing [6].

Various companies are involved in the South African platinum industry with secondary recovery of base metals such as nickel, copper and cobalt forming an integral part of the recovery process. The beneficiation process begins with the underground extraction of the **platinum**-rich ore from mainly the Merensky reef of the Bushveld Igneous Complex, followed by ball milling, concentration and froth flotation. Whether the metal is extracted via the hydrometallurgical or pyrometallurgical process is in principle, immaterial. Each extractive situation must be assessed on its own merits by the consideration of such factors as capital and operating costs and the environmental impact of the two different options that are available [7]. The most common minerals found in the ore are pyrrhotite, pentlandite and pyrite with gangue minerals mainly being pyroxenes. The extraction of the nickel from the ore can be monitored by Mössbauer spectroscopy of the Fe^{2+} and Fe^{3+} components and their relative ratios to each other.

South Africa has coal reserves of more than 30 000 million tonnes; just less than 4 % of the world total, but South Africa is the third largest coal exporting country in the world [8]. A third of the internal use of coal is for its petrochemical industry (Sasol, the largest coal-to-liquids (CTL) producer in the world). The typical iron minerals in coal are pyrite, jarosite, troilite, pyrrhotite, ankerite, illite and siderite [9]. The coal used for gasification and subsequent production of syngas can be characterised and the changes occurring during gasification can be followed by means of Mössbauer spectroscopy [10], where gasification can be defined as the reaction of solid fuels with air, oxygen, steam, CO_2 , or a mixture of these gases at a temperature of over 700 °C to produce synthetic gas that is suitable for use either as a source of energy or raw material for synthetic liquid fuels, chemicals or other gaseous fuels. Catalysts are used in the Fischer–Tropsch synthesis process (FTS) to produce liquid hydrocarbons by converting the synthesis gas from coal gasification in the CTL process, or from natural gas in the gas-to-liquid (GTL) process. Fe-based catalysts offer an attractive option for the CTL process due to their high FTS activity and water-gas shift reactivity which help compensate for the shortage of H_2 in the syngas produce by coal gasifiers. Mössbauer spectroscopy is used for phase identification and for the investigation of the structural and magnetic properties of the Fe-based catalysts which are essential for the understanding of the activity and reactivity of the catalysts during FTS.

2 Experimental

Representative samples for the various industry related investigations were obtained and prepared according to standard procedures. The Mössbauer analyses were conducted on the powdered samples with the aid of a Halder Mössbauer spectrometer capable of operating in conventional constant acceleration mode using a proportional counter filled with Xe-gas

to 2 atm. The samples were placed between Perspex plates and then irradiated with γ -rays from a 50 mCi $^{57}\text{Co}(\text{Rh})$ radioactive source to obtain a room temperature Mössbauer spectrum. The Mössbauer spectrometer was calibrated using α -Fe as the reference and the product species were identified on the basis of their quadrupole and isomer shifts with reference to the values available in the literature [11]. For CEMS analyses a backscatter-type gas flow detector was used. A FEI Quanta 200 ESEM Scanning Electron Microscope, integrated with an Oxford Inca 400 energy dispersive x-ray spectrometer was used for the SEM analyses and a PW1700 Philips x-ray diffractometer with a Cu- K_{α} anode was used for the x-ray measurements. The eddy current apparatus with an absolute probe was employed at a frequency of 10 kHz.

3 Results and discussion

The various industry related investigations will be discussed under separate headings in this section.

3.1 Ferrosilicon

For comparison purposes SEM microphotographs (Fig. 1) were taken of the two FeSi-samples, the one produced by ISCOR, and the other, previously used material, produced by Samancor, South Africa [2]. The composition of the FeSi was 85 wt. % Fe and 15 wt. % Si with minor impurities of Mn and Cr (<1 wt. %), resulting in an ordered phase with a calculated composition of Fe_2Si , consistent with the published data in the ASM Handbook [12]. The average density was found to be 7.18 g.cm^{-3} and the d_{50} size distribution was $\approx 30 \mu\text{m}$ [2].

The Mössbauer spectrum (Fig. 2 left) of the spheroid Fe-Si-samples showed a two-sextet spectrum with a typical 3/2 intensity ratio and hyperfine magnetic field strengths of 19.9 T and 30.7 T respectively, in accordance with literature [13, 14]. For the used non-spheroid FeSi (Fig. 2 right) an additional sextet with hyperfine magnetic field strength of 25.4 T was observed, indicating a possible change in the magnetic properties of the material with the addition of the third sextet possibly attributed to the abrasion process.

In both the plant set-up and in the laboratory experiments the FeSi-slurry formed an initial green coloured froth that changed in time to an oxidised yellow-brown froth and when the froth was removed it was placed between the Perspex plates and subjected to Mössbauer analyses. It was found to be an oxihydroxide complex with parameters as shown in Table 1.

The laboratory tests that were carried out confirmed the $\approx 10 \%$ loss of FeSi-material contributed to the abrasion of the particles. Abrasion of the protrusions of the non-spheroids modified the particles and very small particles were abraded away completely, yielding, in terms of financial losses, a loss of just less than 1 ton/h in the total plant set-up at a cost of about US\$500 per ton. From the results it became apparent that high spheroidal FeSi should be used to minimize FeSi losses [2].

In the case of the recovery of the alluvial diamonds it was also clear that one mechanism of loss of dense medium material was due to abrasion, as mainly angular FeSi is being used [3]. Furthermore valuable mineral losses also occurred at the mine due to the fact that the density of the separation medium changed as more and more of the heavy minerals such as magnetite and ilmenite stuck to the FeSi, which is difficult to separate from the FeSi during the magnetic separation part in the DMS circuit [3]. The Mössbauer parameters for the FeSi

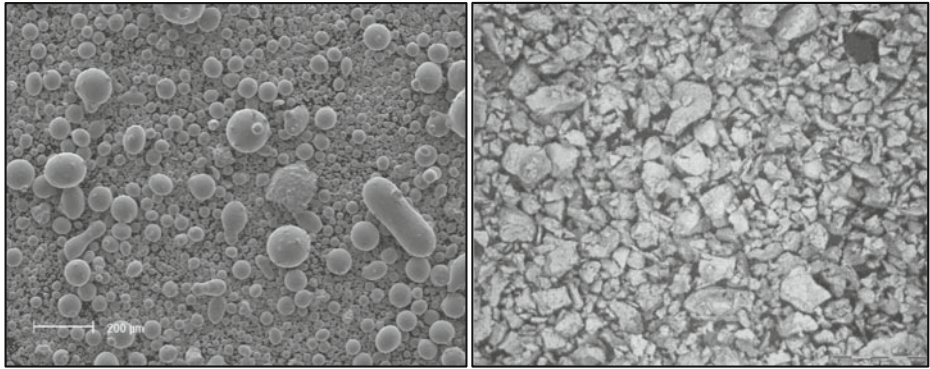


Fig. 1 On the left a microphotograph of the spherical FeSi-material and on the right the non-spheroid material

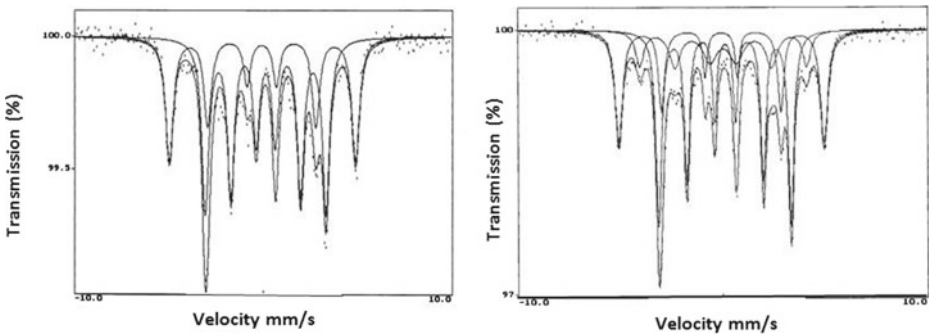


Fig. 2 Mössbauer spectra of on the left the spherical FeSi and on the right the spectrum obtained for the non-spheroid FeSi showing the additional sextet [2]

were similar to the material used at Kumba and the parameters of the magnetite and ilmenite are also shown in Table 1 and their contribution is clearly visible in the spectra (Fig. 3).

3.2 Ferrochromium and nickel recovery

The Bushveld Igneous Complex, South Africa, contains one of the richest sulphide ores in the Merensky reef. Pyrometallurgical extraction is used in conventional sulphide concentrate processing, but due to high costs and pollution problems, hydrometallurgical processing is an attractive method for the selective extraction of valuable base metals, in particular of low grade ores.

The leaching mechanism of a milled Ni-Cu-Co-sulphide ore sample from the Nkomati mine, South Africa, was investigated where the concentrate consisted of the minerals pyrrhotite, pentlandite and chalcopyrite with gangue minerals mostly pyroxenes. The dissolution of the valuable minerals was achieved effectively in a mechanical oxidative pressure-acid medium followed by leaching [15]. From the Mössbauer spectra it was clear that the Ni-bearing pentlandite was leached within the first 15 min, whilst the Cu-bearing mineral, chalcopyrite, was only leached after a period of more than 30 min. The final residue was found to consist mainly of goethite (Fig. 4). After proven laboratory results

Table 1 Mössbauer parameters of the various components for the fresh and/or used FeSi, corrosion product and adhesion minerals [2, 3]

Sample	IS $\text{mms}^{-1}(\pm 0.02)$	QS $\text{mms}^{-1}(\pm 0.02)$	H Tesla (± 0.3)	Relative intensity %
Spheroid FeSi				
Sextet 1	0.04	0.04	30.7	41
Sextet 2	0.23	0.00	19.9	59
Non-spheroid FeSi				
Sextet 1	0.04	0.04	30.7	41
Sextet 2	0.23	0.00	19.9	59
Sextet 3	0.15	0.00	25.4	*
Froth				
	0.17	0.69	—	61
	0.34	0.92	—	29
Magnetite				
Sextet 1	0.38	-0.17	49.9	37
Sextet 2	0.62	0.05	48.1	15
Ilmenite				
	0.97	0.72	—	48

Note: IS = Isomer shift relative to α -iron, QS = Quadrupole splitting and H = Hyperfine magnetic field strength * with the additional 3rd sextet in a spectrum the ratio between the 19.9 T and 30.7 T remained the same, but the 25.4 T sextet has a relative intensity of 22 % with respect to the other two sextets

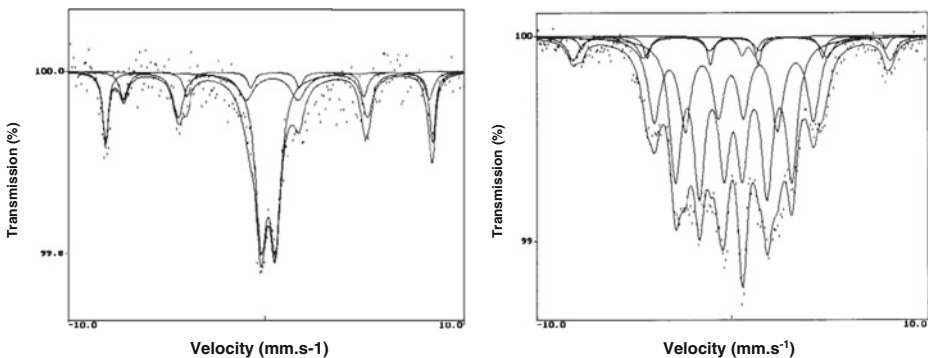


Fig. 3 On the left the Mössbauer spectrum of the feed ore containing magnetite and ilmenite as Fe-bearing heavy minerals and on the right the spectrum of the magnetic concentrate showing, in addition to the Fe-Si, the magnetite and ilmenite [3]

were obtained this hydrometallurgical process was implemented and is still being used at the plant at the Nkomati mine, South Africa.

On the other hand the conventional pyrometallurgical recovery of the base metals is mainly being used in the platinum plants in the Rustenburg area of the Bushveld Igneous Complex, South Africa. Slag and matte samples from furnaces of the various plants have been investigated to understand the high nickel losses that occur and to subsequently improve the recoveries. Anglo Platinum is one of the largest producers of platinum with nickel, copper and cobalt recovered as by-products [16]. The ore is normally upgraded and then melted in an electric furnace with the melt separated in slag and matte, with the matte

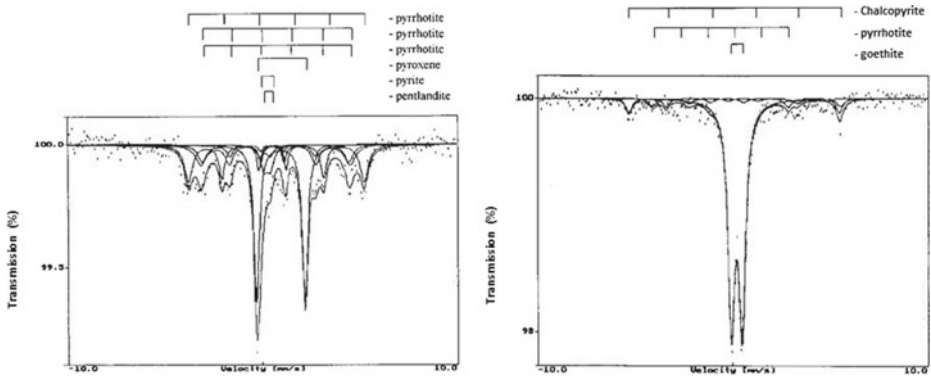


Fig. 4 Mössbauer spectra of the ore sample (*left*) and on the right the spectrum of the leach product after 30 min of leaching

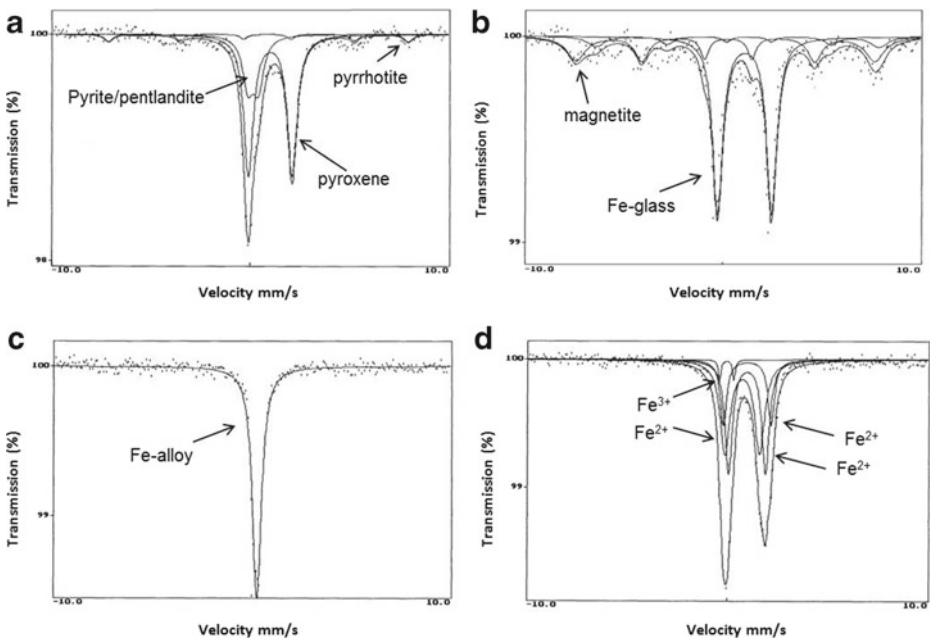


Fig. 5 A Mössbauer spectrum of (a) PGM ore concentrate, (b) slag formed in the flash furnace and sent to the electric cleaning furnace, (c) the spectrum obtained for the matte formed in the flash furnace and (d) the spectrum for the electric cleaning furnace slag

carrying the bulk of the base metals (and PGM's) (Fig. 5). The slag, which is an iron-magnesium-calcium-aluminium-silicate glass, can contain up to 4 % dissolved nickel oxide and has a high (≈ 4.3) Fe^{2+}/Fe^{3+} ratio because of the oxidising conditions in the smelter. The slag is thus treated again in a slag-cleaning furnace where the nickel oxide is reduced with coke and the Fe^{2+}/Fe^{3+} ratio decreases to about 0.02 and leaving less than 0.5 % NiO in the slag. The Fe^{2+}/Fe^{3+} ratio (Table 2), obtained from Mössbauer spectroscopy (Fig. 5

Table 2 Distribution of iron between olivine, glass and magnetite (wt. %) found in the flash and electric furnaces respectively

Sample nr.	Flash furnace				Electric furnace			
	3	5	7	8	1	2	4	6
Olivine (Fe ²⁺)	49 ± 3	44 ± 3	77 ± 3	75 ± 3	70 ± 3	70 ± 3	70 ± 3	70 ± 3
Glass (Fe ²⁺)	10 ± 3	1 ± 1 ?	3 ± 1	4 ± 1	30 ± 10	30 ± 10	30 ± 10	30 ± 10
Magnetite (Fe ²⁺ :Fe ³⁺ = 1:2)	41 ± 3	56 ± 3	20 ± 3	21 ± 2	<dl*	<dl	<dl	<dl
Fe ²⁺ /Fe ³⁺ ratio	2.7	1.7	6.5	6.1	~0.02	~0.02	~0.02	~0.02

*dl – detection limit

Table 3 Mössbauer parameters as obtained for the various Fe-compounds found in the different furnace products

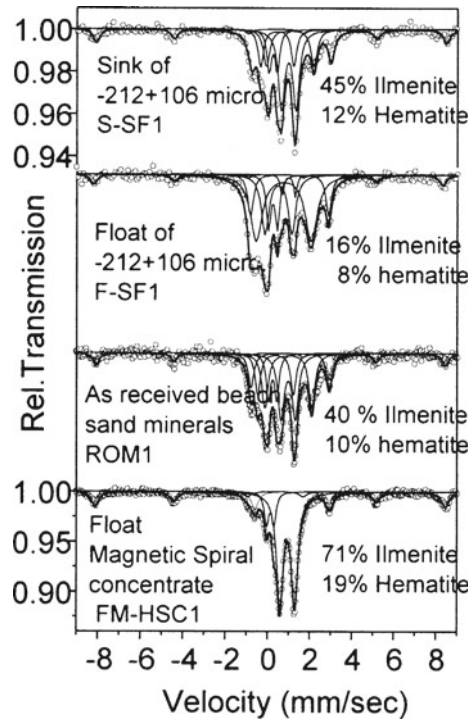
Sample	Component	IS mms ⁻¹ (±0.02)	QS mms ⁻¹ (±0.02)	H Tesla (±0.3)	Relative intensity (%)
Feed (Concentrate)	Doublet 1 Fe ²⁺ pyroxene	1.13	2.21		67 ± 1
	Doublet 2 Fe ³⁺ pyrite/pentlandite	0.28	0.53		25 ± 1
	Sextet 1 pyrrhotite	0.77	-0.35	46.6	8 ± 2
Matte	Singlet (Fe-alloy)	0.41	0.00		100
Flash furnace slag	Doublet 1 Fe ²⁺ Fe-glass	1.11	2.73		66 ± 1
	Sextet 1 magnetite	1.14	-0.61	44.4	12 ± 1
	Sextet 2 magnetite	0.23	-0.15	46.9	22 ± 2
Slag-cleaning furnace	Doublet 1 Fe ²⁺	1.30	2.35		26 ± 3
	Doublet 2 Fe ²⁺ {Fe-glass	1.13	2.04		32 ± 4
	Doublet 3 Fe ²⁺	0.88	1.82		39 ± 4
	Doublet 4 Fe ³⁺	0.06	0.61		3 ± 1

and Table 3) and the amount of magnetite present yielded a valuable tool to ensure optimum nickel recovery [17].

3.3 Mineral recovery from beach sands

The ilmenite (FeTiO₃) remaining in the tailings after the beach sand mining and processing, has a high iron content varying between 30 % and 80 % and makes the use of the ⁵⁷Fe Mössbauer effect useful [5]. The specific gravities of the valuable minerals range between 4.2 and 4.9, while the specific gravities of the gangue minerals are less than 4.0 with main constituent being quartz, having a specific gravity of 2.7. Because of the higher specific gravities of the ilmenite, zircon and rutile these minerals were separated via a wet gravity concentration during the mining operations, with a recovery of approximately 90 % for the heavy minerals mentioned. The beach sand tailings samples, containing some remaining ilmenite were homogenised, riffled, coned and quartered and screened, passing -212 + 106 μm. This fraction was concentrated by means of a spiral column, followed by magnetic

Fig. 6 Room temperature Mössbauer effect spectra of the sink products of the $-212 + 106 \mu\text{m}$ fraction, the float products and the float products after magnetic separation subsequent to the spiral concentration [5]



separation and finally floatation to produce an ilmenite-hematite concentrate with a yield of about 70 % ilmenite and 20 % hematite, with further magnetic separation resulting in the hematite contribution to increase. The float products of the magnetic fraction of the spiral separated products contained about 20 % hematite and only 71 % ilmenite compared to 13 % hematite and 87 % ilmenite in the sink products of the spiral separation [5]. The summarised results are shown in Fig. 6. Screening of the beach sand tailings followed by concentration and magnetic separation, complemented by the floatation process, seemed to be the best route to produce the ilmenite-hematite solid-solution material.

3.4 White cast iron

Ten high chromium (26.5 wt. % Cr, 2.6 wt. % C) white cast iron work pieces were heat-treated to achieve a spread of austenite phase levels. In a first heating cycle, the work pieces were homogenised for 4 h at different temperatures ranging from 690 °C to 1100 °C prior to air-cooling. In a second heat treatment cycle, the samples were first homogenised at 690 °C for 4 h, then destabilised at different temperatures, ranging between 950 °C and 1100 °C and subsequently air-cooled [6].

The CEMS spectra of the heat-treated and air cooled white cast iron samples revealed the presence of two sextets and one single line (Fig. 7). The first sextet, with an internal magnetic field of about 33 T, corresponds to the ferrite ($\alpha\text{-Fe}$) phase of the matrix and the second sextet, with a slightly smaller magnetic field (≈ 27 T), corresponds to a FeCr-alloy. The observed single-line in the Mössbauer spectra was assigned to the retained austenitic phase, which was present in the spectra of samples subjected to both the heat-treatment cycles. The

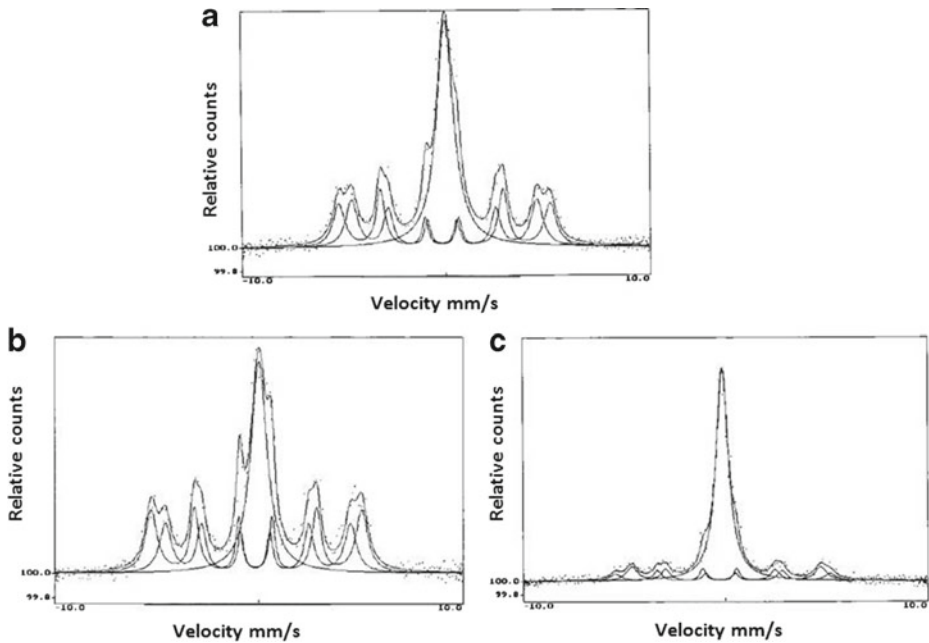


Fig. 7 Typical Conversion Electron Mössbauer (CEMS) spectra as obtained for (a) the sample that was taken for reference purposes, heat treated at 690 °C, (b) the sample heat treated for 1 cycle at 950 °C and (c) the sample that has undergone a two cycle heat treatment, first at 690 °C and then at 1100 °C [5]

retained austenite phase's relative abundance, for the samples subjected to both cycles was the highest at elevated temperature (1100 °C). A (semi)-quantitative analysis of the retained austenite level in the samples was also done with X-ray diffraction (XRD). With the measured Rockwell hardnesses and the results obtained by using an eddy current technique, a comparison with the XRD and CEMS results was made and the calibration of the eddy current apparatus was possible (Table 4). The double cycle heat-treatment process increased the retained austenite percentage with a linear correlation observed between results from eddy current and CEMS, eddy current and XRD and CEMS and XRD measurements as shown in Fig. 8. This portable apparatus can be used in the casting industry during mass production for the retained austenite content determination of the high chrome white iron castings.

3.5 Coal and gasification

With the vast coal reserves available in South Africa and its use in power generation, production of synthetic fuels and weathering problems, the use of Mössbauer spectroscopy is eminent. Only two studies will be mentioned, with the first one dealing with the mineral changes that occur when coal is gasified for the production of syngas and the second one with the subsequent Fischer–Tropsch catalytical process to produce the synfuels. A detailed report on the various coal based research topics conducted in South Africa is found in reference [18].

The coals from the various coal fields in South Africa vary considerably with the coal used for gasification coming from the Mpumalanga/Witbank area in South Africa. It can be described as a sub-bituminous coal with a calorific value of less than 30 MJ/kg and an ash

Table 4 Average values of the relative percentage of the retained austenite phase as determined by XRD and CEMS, hardnesses of the heat-treated white cast iron and eddy current values corresponding to the amount of retained austenite (adapted from [5])

Process	Values of the relative percentage of the retained austenite phase (relative to the sample heated at 690 °C, 7 h)			Parameters	
	XRD %	CEMS	Ave. XRD+CEMS %	Hardness (Rockwell)	Eddy current
One cycle					
690 (7 h)	0	0	0	50.5	130
950 (4 h)	21.5	12	16.75	65.5	202
1000 (4 h)	18.5	14	16.25	67.4	209
1050 (4 h)	19.5	13	16.25	67.5	213
1100 (4 h)	51.5	40	45.75	69.8	231
Two cycles					
690 (4 h), 950 (4 h)	–	25	25	26.5	203
690 (4 h), 1000 (4 h)	–	22	22	17.0	209
690 (4 h), 1050 (4 h)	–	33	33	20.5	219
690 (4 h), 1100 (4 h)	–	49	49	43.0	241

content of up to 30 % with the major minerals present pyrite, quartz, clays and carbonates. The ash fusion temperature (AFT) of a coal source is influenced by mainly silica, iron and sulphur with iron the controlling component influencing fouling and slagging. There is however a constant drive to optimise the gasification process [19] because the fouling and slagging also occurs due to heat induced transformation of not only the Fe-bearing minerals, but also other mineral matter inside the gasifier, which in turn causes undesirable operational conditions, implying a loss in gas production.

The gasifier can be divided into various reactions zones, with the coal entering the top of the gasifier where the coal undergoes drying due to a counter-current flow of hot air and steam from the bottom of the gasifier. As the coal moves down into the gasifier, it experiences an increase in temperature and after the drying zone it enters the reduction zone, then the oxidation zone and finally enters the bottom, the ash is being extracted at the ash grate, with the maximum temperature occurring almost two thirds down the gasifier [20]. Representative samples were extracted, at predetermined positions, with all the samples thoroughly homogenized, riffled and split into equal quarters for investigation in the laboratory.

The only observable Mössbauer mineral in the coal used for gasification was pyrite and decomposition already started in the pyrolysis zone, whilst in the oxidation zone, at the bottom part of the gasifier, oxidation of the iron starts to play a role and hematite formed. In the ash bed the highest temperatures occurred, with peak temperatures well above 1 400 °C and at these high temperatures the SiO₂ and Al₂O₃ also present in the coal agglomerate and form a Fe-containing glass, additional to the hematite previously observed.

Since the catalyst used in the production of the syngases contains iron, various amounts of the used material were added to a laboratory scale apparatus to determine how the AFT would change with an increased amount of iron. To run the gasifiers at lower temperatures will save on energy costs, but on the other hand to run the gasifier at a higher temperature

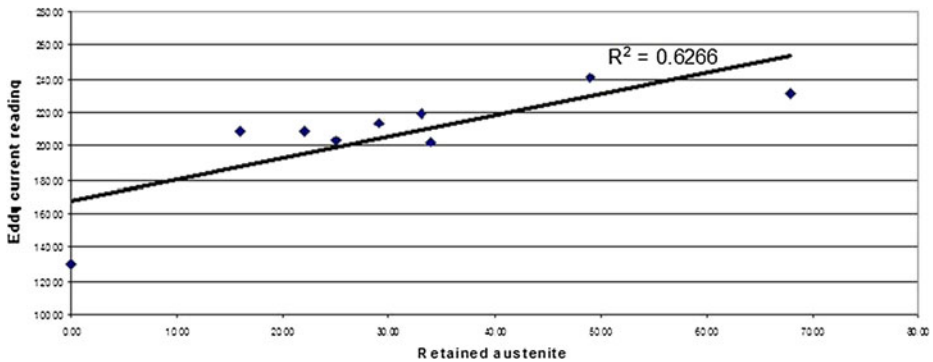


Fig. 8 Correlation between eddy current reading and relative retained austenite abundance (from CEMS and XRD values) [6]

will increase gas production and an optimum condition is always strived for. With only a few wt. % Fe addition the AFT did not decrease too much, but with more than 5 wt. % Fe added to the coal a decrease of more than 200 °C in the AFT was observed, which would be detrimental to the process and currently an investigation is underway to rather look at catalytical gasification by adding alkali salts in small amounts, instead of using the spent catalyst [19].

3.6 Fischer–Tropsch catalyst

The iron-based FT catalyst forms a complex heterogeneous catalyst system comprising of a wide variety of iron oxides and oxyhydroxides. In Figs. 9 and 10 typical Mössbauer spectra of a few Fe-based catalysts are shown. The spectra consist of a two line ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) (Fig. 9a–c), Fe_3O_4 (Fig. 9d–f), CuFeO_2 (Fig. 10a) and $t\text{-CuFe}_2\text{O}_4$ (Fig. 10d).

$\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ is often used as catalyst precursor in low temperature FTS. It is a well-known poorly crystalline material with very small crystallite size (diameter about 2–6 nm) [21] therefore the room temperature Mössbauer spectrum of this species is fitted with two superparamagnetic (SPM) doublets (Fig. 9a) with characteristic of high spin Fe^{3+} species. In Fig. 9a the larger doublet has $\Delta = 1.15$ mm/s which is relatively high for a Fe^{3+} species and is indicative of strongly distorted Fe sites and/or relatively poor crystallinity of the sample [22]. The SPM doublets resolve into sextets at 4.2 K (Fig. 9b) below a blocking temperature (T_B). The Mössbauer spectrum recorded at 4.2 K in an external magnetic field of 10 T (Fig. 9c shows features distinctive of the magnetic state of Fe^{3+} in ferrihydrite. The width of the distribution (measured as the overall standard deviation) of the hyperfine magnetic field at 4.2 K in an external magnetic field of 10 T amounts to about $W_B = 6.5$ T. This value compares well with $W_B \approx 7.8$ T reported for a ferrihydrite sample of poor crystallinity [23]. The large W_B is taken as an indication of a relatively high anisotropy constant in the sample. Changes observed in the intensities ratios in an external magnetic field from the values 3:2:1:1:2:3 expected for the lines 1, 2, 3, 4, 5, and 6, respectively, imply that the spins within a particle are rather fixed relative to each other, but with statistically distributed directions.

Fe_3O_4 on the other hand contains relatively large crystallites as evidenced by the existence of the well resolved sextet at room temperature (Fig. 9d), it is suitable as starting

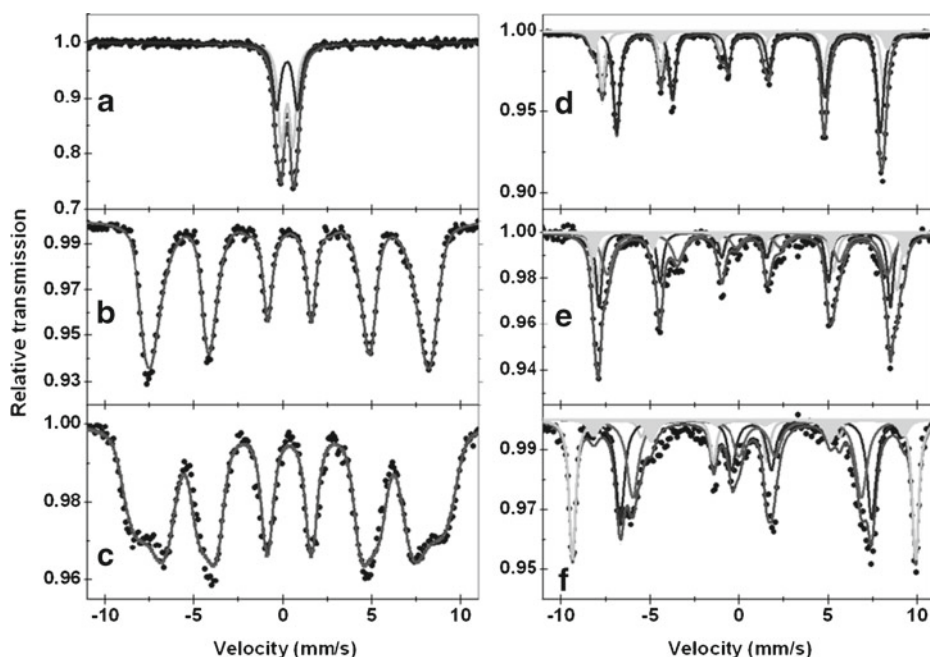


Fig. 9 Mössbauer spectra of 2 line ferrihyrite recorded at (a) 300 K, (b) 4.2 K and (c) 4.2 K in an applied magnetic field of 10 T parallel to γ -rays direction; and Mössbauer spectra of magnetite recorded at (d) 300 K, (e) 4.2 K and (f) 4.2 K in an applied magnetic field of 10 T parallel to the direction of γ -rays. The shaded areas under the absorption peaks in (d)–(f) correspond to hematite impurity

material for high temperature FTS. Above the Verwey transition ($T_V \approx 120$ K) the Mössbauer spectrum of Fe_3O_4 consists of two sextets resulting from the presence of Fe^{3+} on the A sites and a mixture of Fe^{2+} and Fe^{3+} on the B sites. Below T_V (tetragonal structure) an ordered arrangement of Fe^{2+} and Fe^{3+} on the B sites inhibits electron delocalisation [24]. Hence three distinct sextets emerge: one for Fe^{3+} on the A sites, one for Fe^{3+} on the B sites and one for Fe^{2+} on the B sites (Fig. 9e and f). In stoichiometric Fe_3O_4 the ratio of iron species on A and B sites is 1:2 at all temperatures below T_V . The relative absorption areas of the sextets (and the cations distribution) is one third (0.33) for Fe^{3+} on the A sites, one third for Fe^{3+} on the B sites and one third for Fe^{2+} on the B sites. Note the presence of $\alpha\text{-Fe}_2\text{O}_3$ impurity indicating that the Fe_3O_4 sample analysed is partly oxidised.

In Fig. 10a and d the Mössbauer spectra of copper delafossite (CuFeO_2) and copper ferrite ($t\text{-CuFe}_2\text{O}_4$), respectively are shown, also used as catalyst precursors for FTS. In both cases the promoter element (Cu) and the catalytically active element (Fe) are forced to coexist in a single, mixed metal oxide phase, so as to induce an intimate contact between them. The carburisation of CuFeO_2 on exposure to CO produces a mixture of Fe carbide ($\chi\text{-Fe}_5\text{C}_2$ and $\varepsilon'\text{-Fe}_{2.2}\text{C}$) and Fe_3O_4 (Fig. 9b), about 85 % of Fe carbide is in $\chi\text{-Fe}_5\text{C}_2$ form. Upon exposure to syngas during FTS the amount of Fe carbide recedes and the content of Fe_3O_4 increases as a result of oxidation (Fig. 10c).

The reduction of $t\text{-CuFe}_2\text{O}_4$ on exposure to H_2 on the other hand yields $\alpha\text{-Fe}$ (major phase) and Fe_3O_4 (Fig. 9e). Further exposure to CO + H_2 mixture during FTS leads to the formation of Fe carbides (mainly $\chi\text{-Fe}_5\text{C}_2$) while the relative content of Fe_3O_4 (Fig. 9f) as compared to the reduced sample due to oxidation.

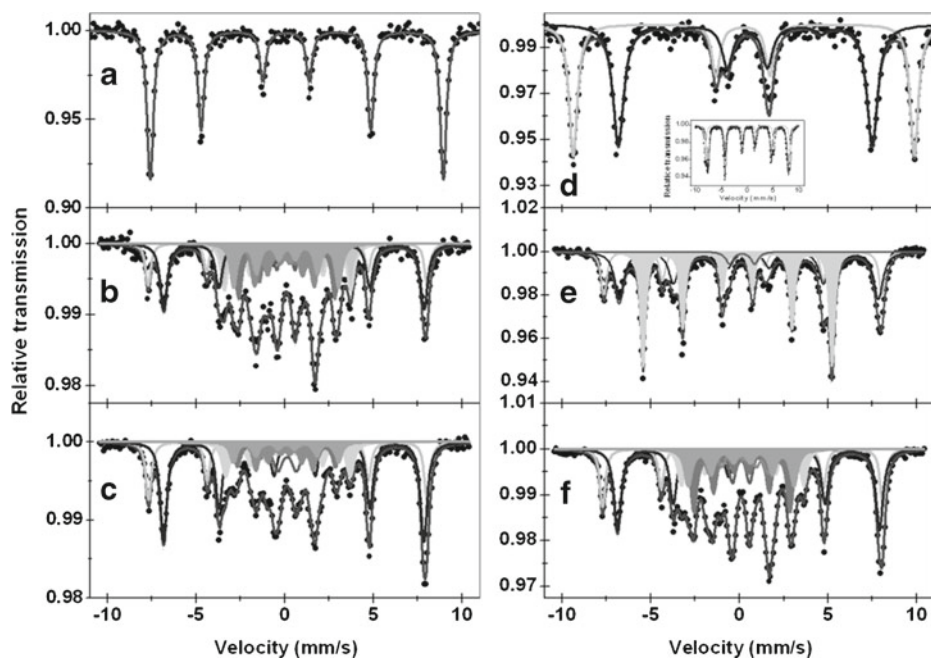


Fig. 10 Mössbauer spectra for (a) CuFe_2O_4 recorded at 4.2 K, (b) CuFe_2O_4 reduced in CO recorded at 300 K, (c) CuFe_2O_4 exposed to FTS after CO activation recorded at 300 K, (d) $t\text{-CuFe}_2\text{O}_4$ recorded at 4.2 K in an applied magnetic field of 10 T parallel to γ -rays direction, (e) $t\text{-CuFe}_2\text{O}_4$ reduced in H_2 recorded at 300 K and (f) $t\text{-CuFe}_2\text{O}_4$ reduced in H_2 and subjected to FTS recorded at 300 K. The insert in (d) shows the spectra of $t\text{-CuFe}_2\text{O}_4$ recorded at 4.2 K. The shaded areas under the absorption peaks correspond to Fe carbides in (b), (c) and (f) and to $\alpha\text{-Fe}$ in (e)

Fe catalysts also contain various levels of supports, such as SiO_2 , Al_2O_3 , TiO_2 , acting as a binder and relatively low amounts of alkali elements such as K are used as chemical promoters and Cu is being used as a reduction promoter. During reduction and FTS there are often strong active metal-support interactions (SMSI) to form for instance Fe silicate species in the case of some Fe catalyst precursors supported on SiO_2 . This often hinders the reduction and adversely affects the performance of the catalyst by holding a fraction of the active metal which otherwise would have participated in FTS. This can also lead to catalyst deactivation. The effects of SMSI and promoters can conveniently be investigated using Mössbauer spectroscopy.

4 Conclusion

One of the main drivers in the South African economy still remains the exploitation of its vast ore reserves. It is clear that although Mössbauer spectroscopy is used on a limited base in this industry, the information gained in the few industrial processes discussed, has helped the industry to better understand the mineral changes and recovery processes to ensure that the industry obtains optimum recovery conditions. Without the use of the Mössbauer effect various products would have gone to waste or lower recoveries would have resulted, with a subsequent loss in income.

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