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The use of Mössbauer spectroscopy in environmental research

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Abstract The impact that mining has on the environment is becoming an ever increasing problem all over the world. South Africa, Brazil and India are main producers of various valuable resources such as for example iron ore, platinum, gold and coal, of which coal and platinum mining will be discussed in this paper. Dumping of ash, waste and discards, result in the formation of acid mine drainage (AMD) due to the high sulphur content of the coal and the waste products. The main Fe-S-bearing minerals in the coals investigated were pyrite, jarosite and ferrous sulphate, a weathering product of pyrite. In the ash produced due to combustion or gasification of the coal, the main Fe-constituents are $Fe^{2+,3+}$ glass ($\approx$30%) and hematite (70%). The amorphous phase of the sample was composed mainly of SiO_2 and Al_2O_3 with trace element inclusions of Hg, Ti, Cd and As. The soil, sediment and overburden in the coal mining areas contain pyrite as Fe-S-mineral and also ferrous sulphate as weathering product, with illite the main clay mineral. From laboratory leaching products of coal and ash, sulphur in the form of SO_4^{2-}, was found to be one of the most leached ions with a concentration ranging between 100–1000 ppm. The amount of Fe leached out from the ash samples was between 2–5 ppm, but the Fe-leachability depends on

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the pH, with higher amounts leached out at pH ≤ 1.5. Magnetite losses, to the amount of about 1kg per tonne of magnetite used, occur during the dense medium separation process (DMS) used in cleaning the coal, which also reports in the waste product. South Africa is the largest producer of platinum and smelting of the ore can lead to various forms of pollution. Magnetite formation in the 2-stage furnace process is used as an indicator of the effectiveness of the reduction and the Fe^{2+} and Fe^{3+} ratio is used to monitor the process. In the flash furnace the ratio is 2–6, whilst in the electric furnace it is ≤ 0.02. If not monitored closely a large amount of nickel loss will occur if sent to the waste dump. Mössbauer spectroscopy was used to identify the Fe-species and the results were augmented by High Resolution-Transmission Electron microscopy (HR-TEM), Field Emission-Scanning Electron Microscopy (FE-SEM)/EDS, X-Ray Diffraction (XRD) and ICP-EOS results.

Keywords Coal · Platinum · Environment · Pollution

1 Introduction

In this paper, coal that is mined in South Africa, India and Brazil and platinum that is mined predominantly in South Africa, are used as examples in discussing environmental problems occurring in mining and processing of these commodities. Since these ores are mined on a large scale and contribute to the economy of these countries, but create environmental problems during the mining and their subsequent beneficiation, refining and utilisation, the environmental process needs further investigation.

1.1 Coal

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 the Gross domestic product (GDP) value [1] and coal exports rank 5th in the world. It is approximated that more than 90% of South Africa's power, about 30% of liquid fuels and 70% of the total energy needs are produced from coal [2]. India has the 4th largest reserves of coal in the world but mining accounted for less than 2% of the GDP in recent years. Notwithstanding this, the coal industry is a key segment of the economy with coal reserves estimated to be about 200 billion tons of which about 80 billion tons are proven reserves [3]. In Brazil the GDP from mining increased to $730 million in the second quarter of 2016 with coal the largest source of non-renewable energy in the country, especially the coal mined in the State of Santa Catarina where the reserves represent about 50% of Brazil's fossil fuels [4]. Coal is highly complex and variable in nature with the inorganic matter dispersed in a random way in the form of mineral inclusions, dissolved salts and inorganic matter often chemically associated with the organic structure [5]. South Africa and India have typical Gondwanaland high ash, high sulphur coals, whilst the coal from Santa Catarina, Brazil, has physical-chemical characteristics that are distinct from other coals, with up to 42% mineral matter and more than 2.2% sulphur [6].

The run-of-mine coal (ROM) has to be beneficiated by means of dense medium separation (DMS) processes to be fit for purpose, creating waste materials that are sent to slimes dumps. Dry beneficiation methods have been developed due to water scarcity in the South African case where magnetite is used in a magnetically stabilized fluidized bed. Some magnetite can however remain behind in the coal and the cleaning residue which in turn can lead to environmental problems as the small particles deposited on the waste dump can become a ubiquitous air pollutant.

This waste, overburden generated during the mining of the coal and ash produced by combustion and gasification, are subsequently exposed to the environment and results in a source of ecological and environmental degradation with AMD formation and were investigated in the present project [6–8]. The chemical formation of AMD occurs when FeS_2 (pyrite) dissolves in rain water in the presence of oxygen as shown by Eq. 1 [9–11] with subsequent possible microbial reaction change of the iron valance shown in Eq. 2 [10] and finally hydrolysis and the formation of the hydroxide (Eq. 3) [9–11] giving the AMD the typical yellow-orange colour.

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+ \tag{1}$$

$$Fe^{2+} + 1/4\,O_2 + H^+ \rightarrow Fe^{3+} + 1/2\,H_2O \tag{2}$$

$$Fe^{3+} + n\,H_2O \rightleftharpoons Fe(OH)_n^{(3-n)+} + nH^+ \tag{3}$$

Experiments using bentonite clay [9] to solve the problems of AMD pollution has shown promising results, but the details will not be discussed in this paper. Besides the inherent mineralogy of the coal to create possible environmental problems, magnetite, lost in the coal cleaning process, can account to a relatively big volume, ending up on the waste dumps, creating additional pollution. No Mössbauer analyses of the magnetite losses have been done previously and were investigated in the present research project.

1.2 Platinum and associated ferrochromium and nickel recovery

Many companies are involved in the South African platinum industry and the secondary recovery of base metals such as nickel, copper and cobalt. The ore from the Merensky reef and/or the Upper Group 2 reef (UG2) of the Bushveld Igneous Complex are mined, milled, concentrated and cleaned by froth flotation. The Fe-S-minerals present in the ore are pyrrhotite ($Fe_{1-x}S$), pentlandite ($(Fe,Ni)_9S_8$), chalcopyrite ($FeCuS_2$), with accessory chromite ($FeCr_2O_4$) and 4–15 g/t platinum-group metals, with gangue minerals mostly being pyroxenes [12, 13].

The amount of magnetite formed in the furnace can be used as an indicator of the effectiveness of the reduction process in the electric furnace to ensure the furnaces are operated at best conditions and the Fe^{2+} and Fe^{3+} ratio is used to monitor the process and to determine the distribution of the iron in the matte and the slag which is formed in the electric furnaces and the self-cleaning furnaces in this typical 2-stage process used [14, 15]. If not monitored closely a large amount of nickel loss, a potential environmental hazardous element, will occur if sent to the waste dump.

2 Experimental

Representative samples for the various industry related investigations were obtained and prepared according to standard procedures.

The proximate analyses of the solid samples were carried out with a Proximate Analyzer (Model: TGA 701; Leco Corporation, USA) by following the ASTM method (ASTM, 1991). The amount of C, H, N were estimated by using an Elemental Analyzer (Model:

Table 1 General physico-chemical properties of coal samples from the three regions investigated

Sample codes		Proximate analysis (% DMF basis)				Ultimate analysis (% as received basis)				CV MJ/kg
		M	Ash	VM	FC	C	H	N	TS	
Coal	RSA	1–5	8–35	10–25	20–60	60–80	4.0–4.8	1.0–2.2	1.2–2.0	17–32
	India	3–7	3–30	30–40	34–50	50–80	4.1–4.6	1.0–1.4	2.2–4.5	24–32
	Brazil	4–17	3–20	30–45	37–46	50–70	4.5–6.1	0.1–1.3	1.5–5.3	16–26

(M: Moisture; Ash: Ash content; VM: Volatile matter; FC: Fixed carbon; C: Carbon; H: Hydrogen; TS: Total Sulphur, CV: Calorific value)

Perkin-Elmer 2400) and the total sulphur by means of a 'Sulphur Analyzer' (Leco Corporation, USA) by applying the ASTM method (ASTM 2013). The nano-mineralogical analysis of the collected coal and coal mine reject solid samples were performed by Field Emission Scanning Electron Microscope (FE-SEM, Model: FEI Quanta^{TM} 650 FEG), integrated with an Oxford Inca 400 energy dispersive X-ray spectrometer and FEI G2 200 KV High Resolution Transmission Electron Microscope (HR-TEM). A FEI Quanta 200 ESEM Scanning Electron Microscope, integrated with an Oxford Inca 400 energy dispersive x-ray spectrometer was also used for the SEM analyses and a PW1700 Philips x-ray diffractometer with a Cu-K$_\alpha$ anode was used for the X-ray measurements. An Agilent 725 Radial ICP-OES instrument was used to measure concentrations of leachants present in the water.

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}Co(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 as well as their hyperfine magnetic fields with reference to the values available in the literature [16].

3 Results and discussion

The two industries-related investigations will be discussed under separate headings in this section. The important process conditions are discussed with the final focus on the constituents causing the environmental effects, which should be avoided.

3.1 Coal

The typical coal physico-chemical properties of coals from the three regions investigated is shown in Table 1 [18–21] and it can be seen the coals are typical sub-bituminous Gondwanaland coals. The sulphur in the coals from South Africa and Brazil occurs mainly as the inorganic mineral pyrite which can result in acidic conditions to form, according to (1). The North-eastern coalfields of India on the other hand have a high (75–90 organically bound sulphur contents with the total sulphur contents ranging between (2–5%).

From the Mössbauer results (Table 2 and Figs. 1 and 5) it was found that the main Fe-S-bearing minerals in the different coal samples investigated were pyrite, jarosite and ferrous

Table 2 Mössbauer parameters of Fe-components found in the coal investigation

Sample	Component	IS mms^{-1} (±0.03)	QS mms^{-1} (±0.03)	H Tesla (±0.5)	Relative intensity (%)
Coal	Pyrite	0.32–0.37	0.62–0.73	–	100
	Pyrite	0.31	0.61	–	12
	Jarosite	0.41	1.07	–	88
	Pyrite	0.35	0.59	–	66
	Ferrous sulphate	1.34	2.95	–	34
Overburden	Pyrite/Marcasite	0.35	0.54	–	61
	Illite	1.05	2.41	–	29
	Pyrite	0.31	0.60	–	8
	Illite	1.22	1.98	–	92
	Jarosite	0.31	0.65	–	68
	Illite	1.21	1.92	–	32
	Pyrite	0.34	0.60	–	87
	Ferrous sulphate	1.27	2.40	–	13
Soil/sediment	Pyrite	0.32	0.57	–	10
	Illite	1.22	1.84	–	90
	Pyrite	0.31	0.66	–	72
	Illite	1.20	1.88	–	28
	Pyrite	0.34	0.67	–	56
	Ferrous sulphate	1.12	2.65	–	44
	Pyrite/Marcasite	0.33	0.56	–	87
	Ferrous sulphate	1.16	2.34	–	22
Coal cleaning residue	Pyrite	0.30	0.61	–	63
	Illite	1.27	2.56	–	15
	Chromite	0.39	1.22	–	3
		1.91	0.39	–	1
	Jarosite	0.34	1.25	–	8
DMS sample	Pyrite	0.31	0.59	–	41
	Magnetite	0.24	−0.08	48.8	21
		0.59	−0.09	46.6	38
Fly ash	Hematite	0.37	−0.17	51.4	62
	Fe^{3+} glass	0.26	0.93		21
	Fe^{2+} glass	1.13	2.14		12
	Jarosite	0.39	1.02		5
	Hematite	0.42	−0.13	51.9	73
	Fe^{3+} glass	0.91	0.83		16
	Fe^{2+} glass	0.26	2.15		11

IS = Isomer shift relative to α-Fe, QS = Quadrupole splitting, H = Hyperfine magnetic field strength

sulphate. In Table 1 an average isomer shift of (0.35 ± 0.03) mms^{-1} and quadrupole splitting of between (0.62 ± 0.03) mms^{-1} and (0.73 ± 0.03) mms^{-1} is shown for all the pyrite in the coal samples investigated and are within known literature values [16]. The Mössbauer

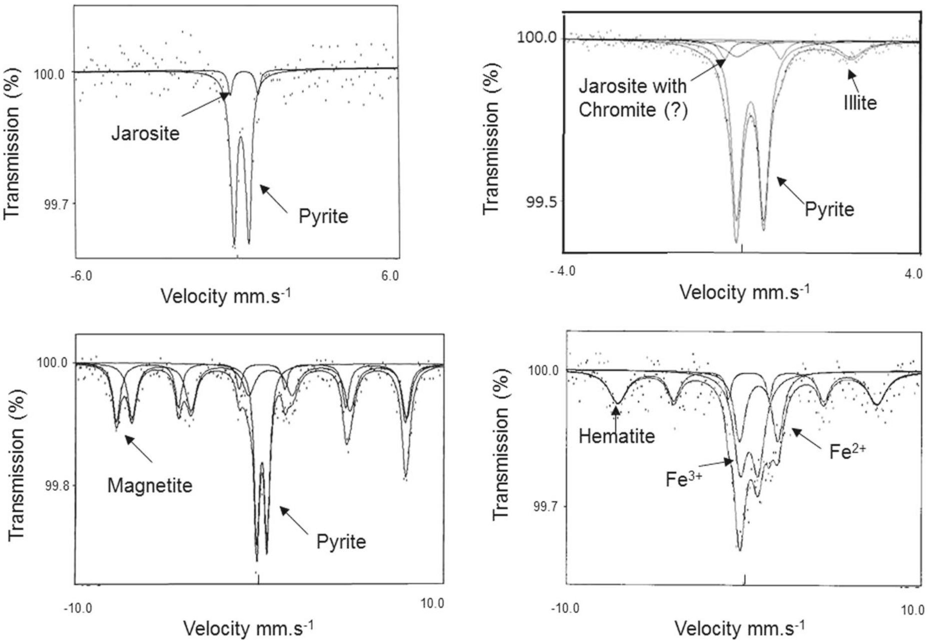

Fig. 1 Mössbauer spectra (*top left*) depicting coal containing pyrite and jarosite (the jarosite most probably comes from pyrite after weathering of the sample) and (*top right*) a coal cleaning residue sample, containing pyrite, jarosite, illite and possible chromite. In (*bottom left*) a spectrum of a DMS cleaned coal sample is shown, indicating that some magnetite remained after the cleaning process and (*bottom right*) a fly ash sample containing hematite and a Fe-glass

parameters of the jarosite and anhydrous $FeSO_4$ are according to those found in literature [16]. In the overburden, soil and sediment, pyrite was found to be the major Fe-mineral present with the clay mineral illite being present in various amounts, depending on the composition of the sample, with quartz the common non Fe-mineral present. Minor amounts of anhydrous $FeSO_4$ were also observed in these samples. In Fig. 1 (top right) a coal cleaning residue sample, containing pyrite, jarosite, illite and possible chromite is shown. Due to the broad line width obtained for the fitting of only jarosite to the Mössbauer spectrum, and the fact that chromite was found in the XRD results of this sample, two additional doublets for chromite were added, giving acceptable line widths. From ICP-EOS results [17] it became apparent that the amount of iron leached from the samples investigated was between 2.5–4.8 ppm, which is a relatively small amount. It should however be noted that the pH of the water in the waste dumps is initially high (between pH 7–9) and only after leaching more of the SO_4^{2-} ions the pH drops much lower ($pH \leq 1.5$), where Fe-leaching becomes much higher and maximum leaching values of 40 ppm were observed in these cases. In Fig. 2 a slimes dam with a low pH is shown, with the typical orange/red colour due to the AMD formation. The amount of sulphur, leached in the form of SO_4^{2-}, ranged between 105–905 ppm and corresponds to the amount of sulphur present in the original sample [17]. Ward et al. [18], noted that between 40 and 80% of the sulphur could be leached, influencing the release of hazardous trace elements such as Hg, Ti, Cd and As (Figs. 3 and 4).

In the ash, produced due to combustion or gasification of the coal, the main Fe-constituents are $Fe^{2+,3+}$ glass (≈30%) and hematite (70%) (Table 2, Fig. 1). The amorphous

Fig. 2 A South African coal slimes dam showing the orange/red AMD formation due to the weathering of Fe-S-containing minerals to Fe-hydroxides

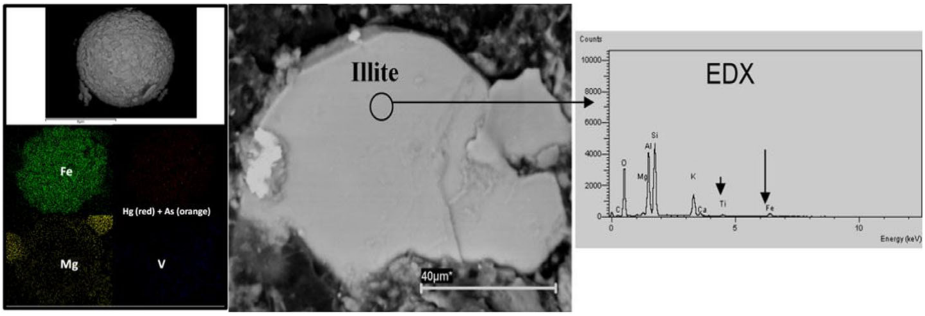

Fig. 3 On the left a spherical hematite particle and hazardous elements in the glassy component in a fly ash sample [19] and on the right an illite grain with inclusions of Ti and Fe is shown in the SEM and SEM-EDX spectrum of a Brazilian coal sample [6]

part of the ash was composed mainly of SiO_2 and Al_2O_3 with varying trace element inclusions observed (Fig. 3). Similar leaching products, as was found in the case of the coal, were observed for the ash samples investigated [17].

Magnetite losses, to the amount of about 1kg per tonne of magnetite used, occur during the dense medium separation process (DMS) used in cleaning the coal, which also reports in the waste product. A Mössbauer spectrum of a coal sample containing pyrite and jarosite, is shown in Fig. 1 (top left) and the cleaned product (Fig. 1 bottom left) contains in addition to the pyrite, magnetite as well. Due to the small amount of jarosite present it was not observed in the cleaned product. The magnetite does not present an environmental or human health concern, unless inhaled as it is stable in normal weathering conditions (Fig. 5).

3.2 Platinum and associated ferrochromium and nickel recovery

The platinum ores mined in South Africa are beneficiated either by pyrometallurgical or hydrometallurgical means. The average chemical composition of the feed ore, the two furnace products and the slag cleaning residue, as determined by XRD analyses, is given in Table 3, showing the high amounts of iron and when mainly in the Fe^{3+} state leads to subsequent loss of Ni. From the Mössbauer results the mineral composition of the ore is shown in Fig. 6, consistent with the chemical composition, as determined by XRD.

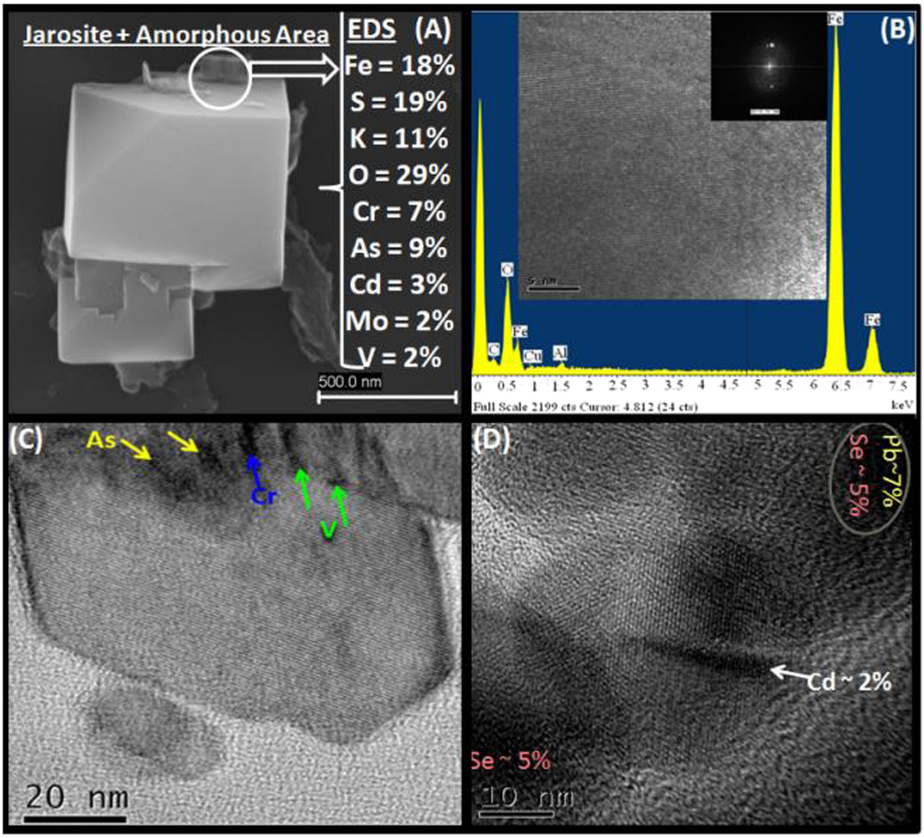

Fig. 4 Fe-nano-minerals can contain hazardous elements such as shown in the *top left* of a FE-SEM image of jarosite and the amorphous area around the jarosite of an Indian coal with the chemical composition also indicated. In the *top right* the XRD spectrum of hematite in an Indian fly ash sample is shown and in the *bottom left* and right HR-TEM images of goethite and magnetite in a fly ash sample respectively [20]

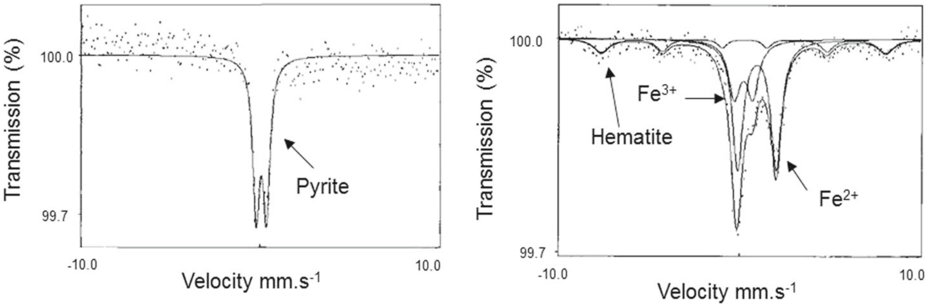

Fig. 5 Mössbauer spectra of (*left*) coal containing only pyrite used for gasification and (*right*) the final ash product formed after gasification, containing a $Fe^{2+,3+}$-glass and hematite

Ferrosilicon (FeSi) is used in the DMS operations to separate the gangue materials from the valuable ore. The FeSi is reclaimed from the process stream for re-use by means of

Table 3 Chemical properties of components from the PGM-experiment as determined by XRD analyses

Sample	MgO	Al_2O_3	SiO_2	CaO	Cr_2O_3	Fe	Co	Ni	Cu	S
Feed ore	13.8	3.9	33.3	3.5	1.3	18.4	0.1	4.2	2.7	10.1
Electric furnace	<0.3	1.3	<0.2	<0.2	1.0	40.0	0.4	16.8	10.7	28.4
Revert furnace	4.3	2.9	17.8	1.9	3.6	26.7	0.3	15.6	8.7	9.9
Slag cleaning furnace	21.5	5.3	46.7	8.3	1.4	10.8	0.02	0.1	0.1	0.3

In addition in the slag is Na_2O (0.38) and K_20 (0.23)

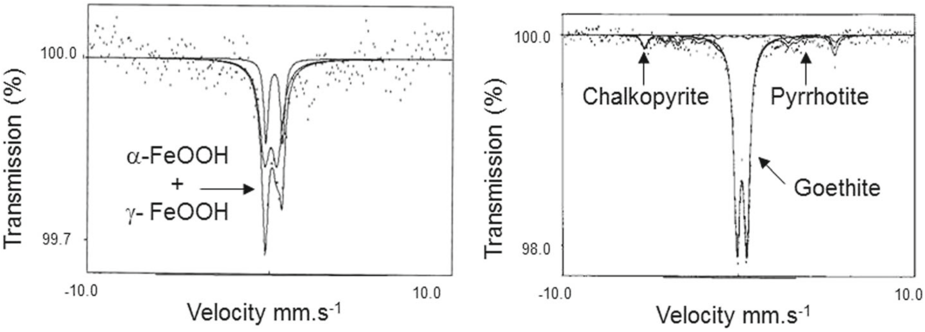

Fig. 6 Mössbauer spectra of (*left*) froth and (*right*) final leachate products remaining in the leaching of a Ni-Cu-Co-sulphide

magnetic separation where a slurry is made with the FeSi and water to obtain the correct density medium for separation [21]. With abrasion of the FeSi in the beneficiation process a froth, greenish in colour, typical of Fe^{2+}-ions in water, formed, which in time changed to a yellow-brown Fe^{3+}-oxide with exposure to air. It was found that both β-FeOOH and γ-FeOOH were present in the froth (Fig. 6), with the biggest loss of the Fe-Si-material due to the abrasion of the particles, with a loss of about 0.5 kg/ton occurring [22]. Albeit in small amounts, it causes environmental degradation as the Fe released with other hazardous minerals such as chromite also end up on the waste dumps.

For the hydrometallurgical process, the Ni-Cu-Co-sulphide ore was successfully dissolutioned in a oxidative pressure-acid medium followed by leaching [23]. It was reported [23] that, in addition to the minerals mentioned, magnetite was also identified in the float sample as an additional mineral, but due to the low relative abundance (4%) it was not detected in the ore sample. This assumption was wrong as a follow-up investigation showed that magnetite and not FeSi was used in the DMS process and the magnetite found was actually the result of magnetite loss to the float material in the DMS process, similar to the case discussed for the coal. In the final stage of leaching the remaining residue was found to consist mainly of goethite (Fig. 6) and being dumped on the waste dams, causes the possible formation of AMD.

In the pyrometallurgical process, ore, matte, reverts and slag samples were investigated to understand the high nickel losses that occur and to subsequently improve the recovery of the nickel, thus reducing nickel products finding their way to waste dumps, contributing to

Table 4 Mössbauer parameters of Fe-components found in the platinum and associated ferrochromium and nickel recovery products or by-products

Sample	Component	IS mms^{-1} (± 0.03)	QS mms^{-1} (± 0.03)	H Tesla (± 0.5)	Relative intensity (%)
Froth	$\alpha + \gamma$-FeOOH	0.28	0.51	–	63
		0.38	0.63	–	27
Leachate	Pyrrhotite	0.62	0.18	30.3	6
	Chalcopyrite	0.35	−0.02	33.5	11
	Goethite	0.32	0.86	–	83
	Pyrite	0.35	0.59	–	66
	Ferrous sulphate	1.34	2.95	–	34
Feed ore	Pyrrhotite sextet 1	0.63	0.18	28.1	25
	sextet 2	0.61	0.15	23.8	18
	sextet 3	0.61	0.16	23.5	10
	Pentlandite	0.36	0.34	–	7
	Pyrite	0.35	0.52	–	5
	Pyroxene	1.06	2.50	–	35
Electric furnace	Singlet (Fe-alloy)	0.41	0.00		100
Revert furnace	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

IS = Isomer shift relative to α-Fe, QS = Quadrupole splitting, H = Hyperfine magnetic field strength

pollution problems as it is a carcinogenic material. The Mössbauer parameters obtained for the various products are shown in Table 4.

The main minerals in the ore were pyrrhotite, with secondary minerals pentlandite, chalcopyrite, chromite and the PGM-group of metals. The gangue material mainly consisting of pyroxenes (Fig. 7 top left). The concentrate is melted in an electric furnace with the molten material separated in slag and matte, with the matte containing the base metals in a Fe-Cr-Ni alloy, including the PGM's (Fig. 7 top right). The slag has a high Fe^{2+}/Fe^{3+} ratio of between 2 and 6 and can contain up to 4% dissolved nickel oxide (Fig. 7 bottom right) because of the oxidising conditions in the smelter. The slag is subsequently treated in a slag-cleaning furnace where the nickel oxide is reduced with coke and the Fe^{2+}/Fe^{3+} ratio (Fig. 7 bottom left) decreases to about 0.02 and leaving less than 0.5% NiO in the slag. The Fe^{2+}/Fe^{3+} ratio, obtained from Mössbauer spectroscopy and the amount of magnetite present yielded a valuable tool to ensure optimum nickel recovery [15] and minimum environmental pollution. In Fig. 8 a SEM micrograph is shown of the slag with magnetite inclusions, which formed in the cleaning furnace (right) and on the left in the figure a chalcopyrite and pentlandite crystal is shown after leaching of the ore, showing the different stages of dissolution in the leaching of the ore.

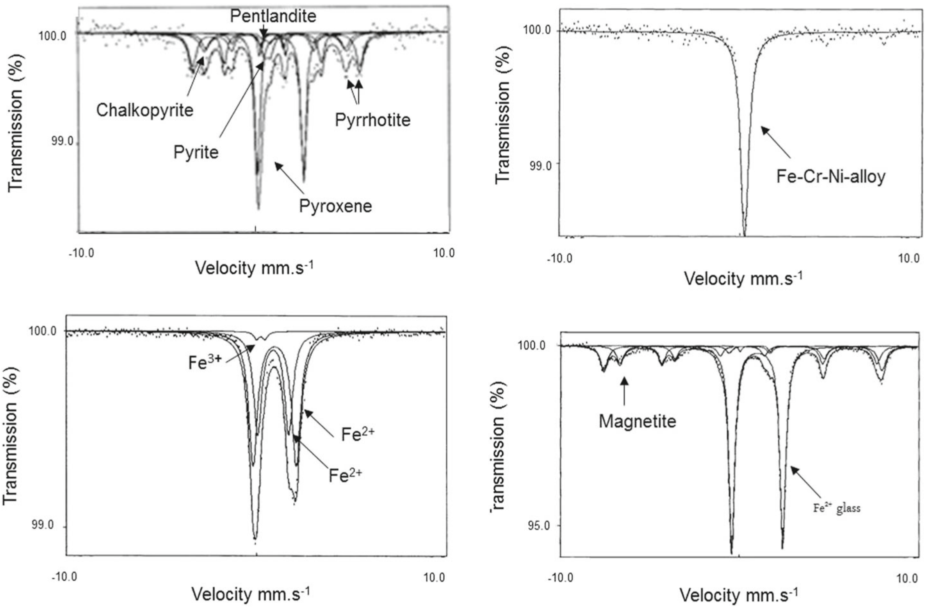

Fig. 7 Mössbauer spectrum of an ore sample (*top left*) found in the Bushveld Igneous complex and the spectrum of the Fe-Cr-Ni-alloy formed in the electric furnace (*top right*). The spectrum for the electric furnace slag showing a high Fe^{2+}/Fe^{3+} ratio (*bottom left*) and the spectrum of the slag from the slag-cleaning furnace and in the bottom right showing magnetite and almost no Fe^{3+} indicating minimal loss of Ni

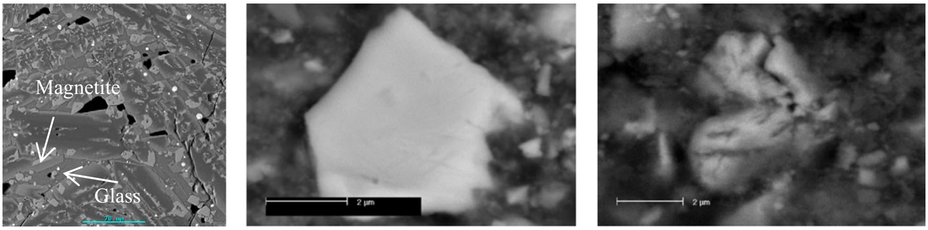

Fig. 8 On the left a backscattered electron image of the slag containing magnetite [23]. On the right an euhedral chalcopyrite particle (*left*) and a pentlandite particle (*right*) after leaching, showing almost complete dissolution of the latter [23]

4 Conclusion

One of the main drivers in the three countries economies still remains the exploitation of their vast ore reserves. Mössbauer spectroscopy is not used often as a tool to monitor the processes and with the addition of special characterising techniques such as SEM, SEM/EDAX, HR-TEM, helped to broaden the information gained in the industrial processes discussed and for the industry to better understand the mineral changes and recovery processes to ensure that the industry obtains an optimum recovery condition and ensuring minimum pollution effects to occur. Pyrite has been found to be the main Fe-bearing mineral in all coal samples and the dissolution creates the Fe^{3+} and SO_4^{2-} that causes the AMD formation. Containment of these minerals, when dumped on waste dumps, has to be done in such a way to minimize any pollution problems. Neutralising the AMD with lime or limestone is only a short term solution as acidification is only slowed down and present investigations show positive results when bentonite clay is used to contain all leached species in a neutral pH environment. In the platinum industry, chromite, containing a large amount of iron, is a typical refractory ore and in addition to the other Fe-bearing minerals present, the Fe^{2+}/Fe^{3+} ratio is used to ensure that Ni in the ore is not lost to the waste, but optimally recovered.

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