Iron bearing minerals characterised with Mossbauer spectroscopy at the Mineral Processing and Technology Research Centre, University of Johannesburg, South Africa.

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Abstract. Platinum group metals reserves have been mined in South Africa using the Merensky, UG2 and Plaatreef reefs. Recently the UG3 seams containing planar chromite platiniferous ore materials have been uncovered in the Uitkomst complex. The understanding of their mineralogy would inform on the processing and concentration routes to take leading to the recovery of associated base metals and to the production of platinum group elements therefrom. Base metals from such a feed are produced mainly through a dissolution process in acidic media. The knowledge of associated iron minerals informs on whether or not reductants or oxidants should be used before iron removal from the solution commonly by precipitation. ^{57}Fe Mossbauer spectroscopy has been extensively used at the mineral processing and technology research centre of the University of Johannesburg. Iron Mossbauer spectroscopy has been crucial in elucidating the presence of the two sites for Fe^{2+} and other two sites for Fe^{3+} in the flotation concentrate while only one site of Fe^{3+} and one site of Fe^{2+} were observed in the feeding ore. The existing gangue materials in the ore might have hindered the accessibility of the gamma by the probe. From the Mossbauer spectra obtained, one was able to determine the efficiency of the ferromanganese reduction process with coke and appreciate the effectiveness of the roasting of the nickel sulphide concentrate. An assessment of chromite types in the UG3 materials was achieved through then determination of the Fe^{3+}/Fe^{2+} ratios.

1. Introduction

Iron Mossbauer spectroscopy, a recoilless resonant emission and absorption of gamma rays where iron is used as a probe, has been used in earth science, materials development, materials characterisation and in monitoring of processes. Geology, chemistry, catalysis, materials engineering and science, even physics have been fields for its application. Up to the mid-eighties Gonser [1] extensively used the Mossbauer spectroscopy in physical metallurgy where phase transformations in steels and ferrous materials were investigated. The application of the Mossbauer spectroscopy in mineral processing or in metal extraction has been scarce. The Mineral Processing and Technology Research Centre from the University of Johannesburg was established in the late nineties for the training of postgraduate students and for service to the local mineral industry. In the past seventeen years, Mossbauer spectroscopy has been introduced to students at the metallurgy department where by-products generated during the drilling of hematite ore with tungsten carbide drill bits were simulated. Nanomaterials generated by mechanically alloyed minerals were also investigated. Since then the mineral processing and technology research centre has focussed its efforts on the mineral characterisation using Mossbauer spectroscopy in addition to the conventional x-ray diffraction, Fourier Transform Infrared spectroscopy, X-ray fluorescence and atomic absorption spectroscopy with the scanning electron microscopy.

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2. Mossbauer spectroscopy in mineral processing and value recovery

As demonstrated in numerous technical confidential reports, published journal articles [2,3 and 4] and students dissertation/thesis, the effectiveness of the beneficiation and processing of minerals prior to the recovery or extraction of metals contained therein could be monitored with iron Mossbauer spectroscopy. Froth flotation of sulphide ores to produce concentrates or the conversion of sulphide minerals into their oxidised form through roasting could be followed by analysing the hyperfine interactions parameters of Mossbauer spectra of the crystalline as well as non-crystalline phases formed in the materials. Minerals enrichment through either magnetic separation or through gravity separation could be monitored. In collaboration with colleagues, it was interesting to see how Mossbauer spectroscopy could add value to the processing of locally found minerals in South Africa. Additionally, reported data on gold Mossbauer and on the application of Mossbauer spectroscopy to coal research are available [3, 6]. Platinum Mossbauer would be the future of Mossbauer spectroscopy in a mineral rich country such South Africa.

3. Materials and methods

Room temperature Mossbauer spectroscopy, in transmission mode with a ^{57}Co gamma rays source, was used. Locally found ores, concentrates or tailings were used while the efficiency of selected metallurgical processes was evaluated, and the quality of generated products was assessed using related hyperfine interactions parameters be it the isomeric shift, the quadrupole splitting or the magnetic field. Simulated plant treatment, processing and beneficiation processes of minerals were conducted at laboratory scale while some feeds were directly obtained from the production.

4. Minerals characterisation using Mossbauer spectroscopy at the Mineral Processing and Technology Research Centre.

Mossbauer spectroscopy has been used for the coal industry to identify and differentiate coal seam products as well as coal origins. The proportion of related coal iron bearing minerals (sulphate, pyrite or marcasite, clays) has been a decisive indicator [2] of a good coal in addition to the calorific contents, the ash content and the sulphur content. The coal abrasiveness index value should be related to the hyperfine interaction parameters. Mineral phase transformations occurring during the use of coal, gasification or pyrolysis have been investigated [2]. Mossbauer has also been used in the characterization of natural chromite samples from the Bushveld complex South Africa. The Fe^{3+} /Fe^{2+} ratios were determined. Two different types of chromites were identified and reported [3]. Type 1 chromites have low Fe^{3+}/Fe^{2+} ratios (between 0.2 and 0.4) and contains 3 cations for every 4 oxygen ions in the chemical formula while type 2 chromites have high Fe^{3+}/Fe^{2+} ratios (between 0.7 to 1.3) and contains less than 3 cations per oxygen ions in the formula). As noticed in this paper (Figure 1 and Table 1), Ferromanganese ores of different manganese contents (36 % and 44%) were studied with Mossbauer spectroscopy. From the lower manganese content ore only a super ferromagnetic doublet was observed while the ore with a higher manganese content showed the presence of an extra iron oxide which would possible be a hematite. The two manganese ores were reduced with metallurgical coke in a tube furnace at temperature between 1300^0C and 1400^0C. Mossbauer spectra (Figure 1) of the reduction products showed a Fe^{2+} component in both cases. Hematite contained in the 44% manganese ore (spectre ore 44) has been completely reduced into a simple oxide.

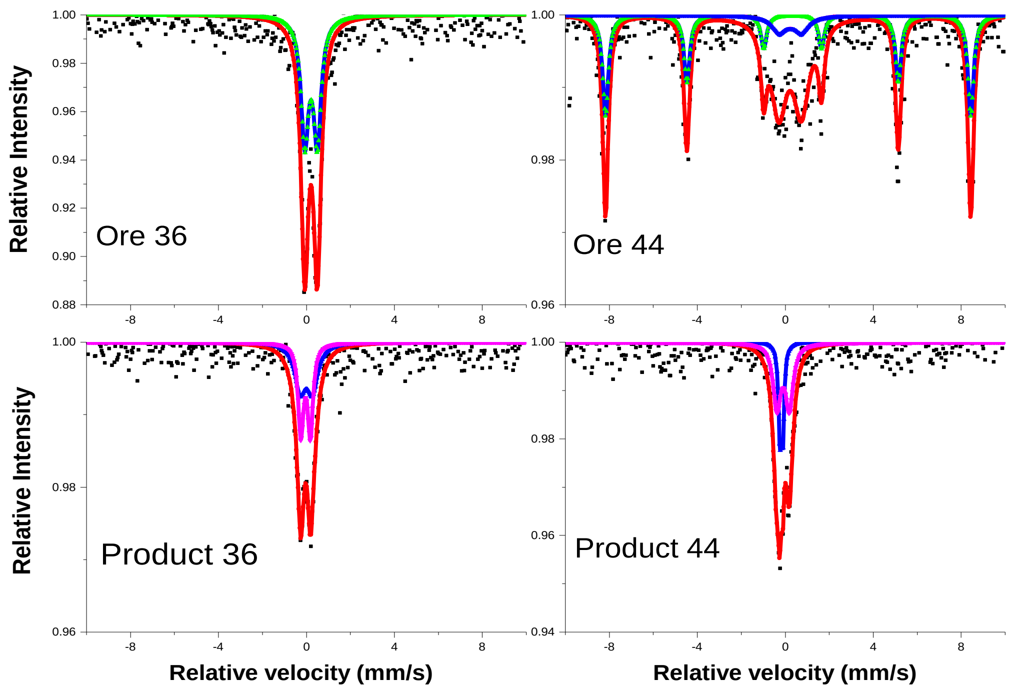

Figure 1. Mossbauer spectra of ferromanganese ore samples (Ore 36 and ore 44) and their reduction products with metallurgical coke in a tube furnace. The iron oxide contained in the ore 44 has been reduced as typified by only a superparamagnetic doublet in the spectrum of the product 44.

Table 1. Mossbauer parameters of ferromanganese ore samples and products from reduction.

Ferromanganese Ore	Isomeric shift δ_{Fe} **(mm/s)**	Quadrupole splitting **(Δ) (mm/s)**	BHF **Tesla (T)**	Fe^{3+}or Fe^{2+}	Abundance **(%)**
	0.36	-0.20	51.5	Hematite	62
Ore 44	0.35	1.03	----	Fe^{3+}	38
Reduction	-0.06	0.13.	----	Fe^{3+}	16
Product 44	0. 03	0.57	----	Fe^{2+}	84
Ore 33	0.33	0.57	----	Fe^{3+}	100
Reduction	0.12	0.56	----	Fe^{3+}	67
Product 33	0.09	0.44	----	Fe^{3+}	33

5. Mossbauer characterization of PGM containing chromite samples from the Bushveld complex
South Africa has the highest reserves of chromite which are approximately greater than 75% of the world's economic resources. All of these resources are mined from the Bushveld complex were several Chromite seams exist. The economically rich seams are the lower group seams, middle group 1 and 2 seams and the UG2 seam (upper group 2). The last of these is not of interest as a source of chromite alone but primarily as a source of platinum group metals (PGMs). A bulk of South African

chromite supply is from PGM producers since after the processing of the PGMs by froth flotation, the chromite is recovered from the tailings of the PGMs at a grade of approximately 45% Cr_2O_3 by means of gravity separation, making the tails easy and cheaper to extract chromite from them. In recent years, due to excessive exploitation PGM content of the UG2 Chromite seams is depreciating, PGM producers are slowly turning to the newly found UG3 seam for PGM production, characterization processes of the new seam are currently under way. Characterization of the newly discovered Bushveld complex UG3 seam ore and its froth flotation products was performed using Mossbauer spectroscopy technique and below are the Mossbauer spectra obtained from their analysis, together with the summary of their results showing, the isomer shift, quadrupole splitting, Fe oxidation states and % Fe abundance in the samples (Figure 2 and Table 2).

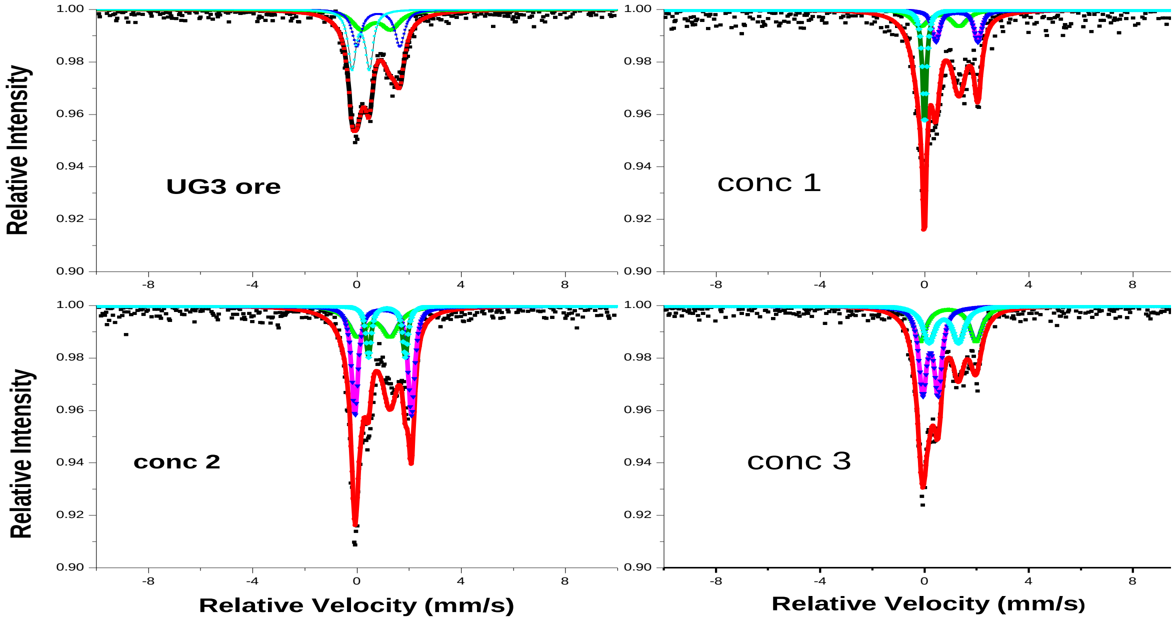

Figure 2. Mossbauer spectra of UG3 Chromite samples

MS spectra of UG3 ore samples and those of the flotation product looked similar but the difference is in the abundances of the Fe^{3+} and Fe^{2}+. UG3 ore has a ratio of 0.3 making it type 1 chromite. The concentrate 1 has a Fe^{3+}/Fe^{2+} ratio of 0.2, which indicates that it has high abundance of Fe^{2+} .The concentrate 2 has a Fe^{3+}/Fe^{2+} ratio of 1.4, making it a type 2 chromite and the concentrate 3 has a ratio of 0.5 making it a type 2 chromite.

From the UG3 chromite spectra (Figure 2), it was found that the ratio of the Fe^{3+} /Fe^{2+} in the ore is +-0.3, showing a high content of Fe^{2+} in the divalent site. Mossbauer has also been used in the characterization of natural chromite samples from the Bushveld complex South Africa. The Fe^{3+}/Fe^{2+} ratios were determined. Two different types of chromite were identified. Type 1 chromites have low Fe^{3+}/Fe^{2+} ratios (between 0.2 and 0.4) and contain 3 cat-ions for every 4 oxygen ions in the chemical formula, type 2 chromites have how Fe^{3+}/Fe^{2+} ratios between 0.7 to 1.3 and contains less than 3 cat ions per oxygen ions in the formula [3]. From the Mossbauer spectroscopy UG3 ore samples Fe^{3+}/Fe^{+2} ratio it can be said that the UG3 ore is the type 1 Chromite in the Bushveld complex.

Chromite from PGM ore processing and vanadium tailings from ferro-vanadium ore, copper converter slag from BCL and iron ore from Thabazimbi were characterized using Mossbauer spectroscopy at the Mineral processing and technology research centre. Iron ore was characterized by a magnetic sextet at room temperature. The copper smelter slag as well as the titanium slag showed iron in two sites as Fe^{2+} [4].

Table 2. Mossbauer parameters of UG3 Chromite samples

Ferromanganese Ore	Isomeric shift δ_{Fe} (mm/s)	Quadrupole splitting (Δ) (mm/s)	BHF Tesla (T)	Fe^{3+}or Fe^{2+}	Abundance (%)
	0.86	-1.13	----	Fe^{3+}	50
UG3Ore	0.94	1.65	----	Fe^{3+}	25
	0.26	0.67	---	Fe2+	25
UG3conc1	0.71	1.49	----	Fe^{2+}	57
	1.36	1.61	----	Fe^{2+}	28
	0.31	----	----	Fe^{3+}	15
	0.77	1.25	---		58
UG3conc2	1.12	2.17	----	Fe^{3+}	32
	1.27	1.41	-----		10
	1.03	2.14	-----	Fe^{2+}	34
UG3conc3	0.34	0.59	----	Fe^{3+}	32
	0.85	1.14	----	Fe^{2+}	34

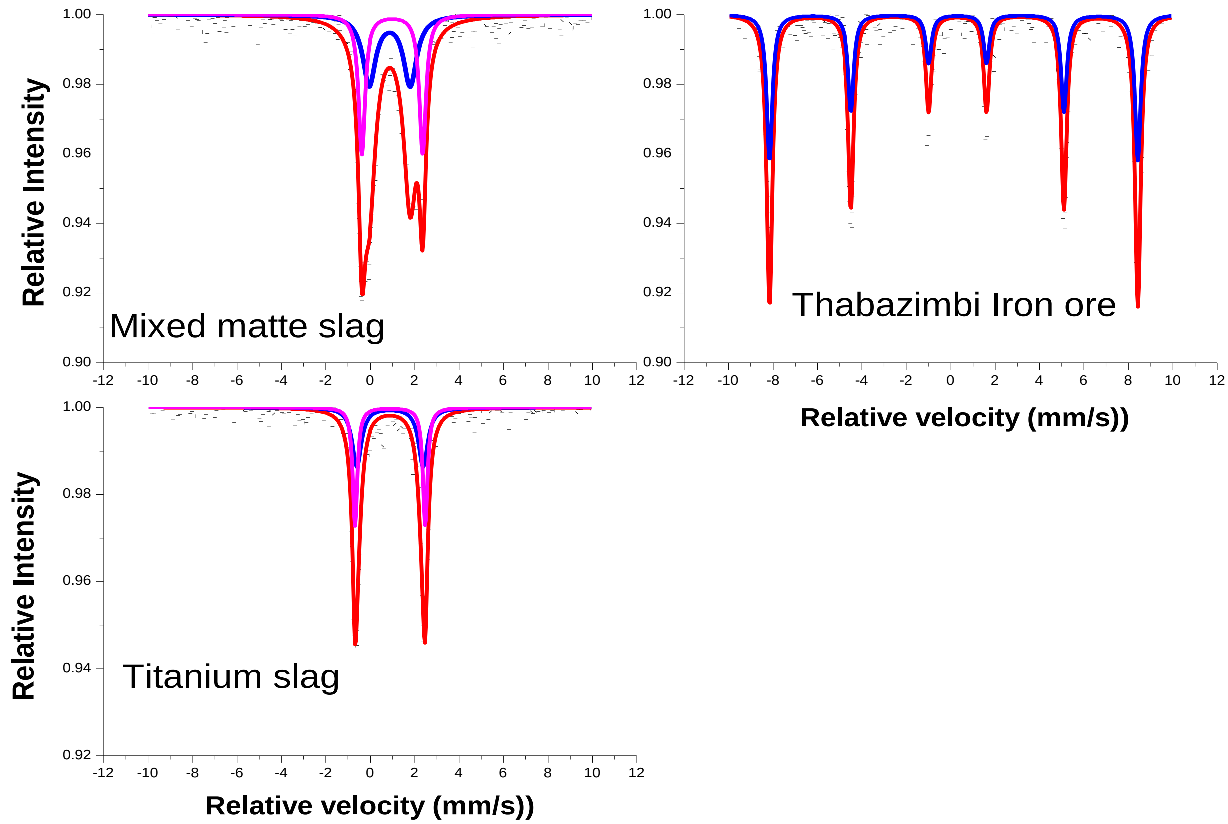

Figure 3. Various mineral processing materials

Mossbauer parameters of the Thabazimbi iron ore (Figure 3 and Table 3) reveal that the iron oxide in the studied ore is mainly hematite with an internal magnetic field of 51.1 Tesla.

Table 3. Mossbauer parameters of various mineral processing materials

	Isomeric Shift **(δ/Fe)+-0.01**	Quadrupole splitting **(Δ) +-0.01**	BhF	ion	% abundance
	0.81	0.96	----	Fe^{3+}	48
	0.26	0.65	---	Fe^{3+}	29
Chromite	0.92	1.56	----	Fe^{2+}	24
Iron ore Thabazimbi	0.35	-0.18	51.6	Fe^{3+}	hematite
Titanium	1.01	2.99	---	Fe^{3+}	66
Slag	1.02	3.17	---	Fe^{3+}	34
Matte-slag	1.00	1.85	---	Fe^{3+}	67
Mixture	1.11	2.76	---	Fe^{2+}	33

Nkomati mine in Mpumalanga produces nickel concentrate through froth flotation. Further beneficiation of base metal bearing minerals has being done using pyrometallurgical routes, these days hydrometallurgy is becoming an attractive tool because of the high thermal costs and pollution problems associated with Pyrometallurgy [2]. Mossbauer spectroscopy was used to characterize the products of roasting of the Nickel sulphide concentrate prior to leaching with sulphuric acid and hydrochloric acid [4].

6. Challenges of Mossbauer spectroscopy training at postgraduate level

Mossbauer spectroscopy is a delicate characterisation technique using nuclear transition leading to the emission of gamma rays which selected are resonantly absorbed by an absorber/sample conveniently prepared. The interpretation and discussion of the data obtained require a good understanding of the hyperfine interactions parameters (isomeric shift, quadrupole splitting, magnetic field etc…) and an insight on the material under the study. Often the type of candidate available to tackle the intrinsic and holistic comprehension challenge from this technology constitutes a problem. The understanding level of quantum and nuclear physics required from the candidate to comprehend the basics and fundamentals of the related interactions is often above the average of commonly encountered candidates. The technology and relevant nuclear spectrometer components also become very expensive.

7. Conclusion

Mossbauer spectroscopy is a characterization technique like any others. It can add value into the information or analysis obtained from other techniques. It supports and complements information from other techniques. From Mossbauer results South African chromites could be classified as type 1 or type 2. The reduction of the ferromanganese ores with coke could be easily monitored with the MS study. This paper shows data on the UG3 ore. It is for the first time that Mossbauer study of UG3 has been reported. From the research and analysis performed in this project, it was shown that one can monitor mineralogical phase transformations that are taking place in different mineral processing applications; it was also shown that Mossbauer spectroscopy can differentiate between types of ores and similarities between clays of different origins.

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8. References

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