

Inventory Assessment of the cleaning of Plant Off-gas in the recovery process of PGM at the Anglo American Platinum LTD, South Africa

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Abstract

The cleaning of off-gas in the process of producing platinum group metals and the conversion of highly concentrated Sulphur dioxide (SO_2) to sulfuric acid (H_2SO_4) are crucial in the current discussions for attempting to reduce emissions in the entire process of mining platinum metals in South Africa. Emissions of SO_2 gas into the atmosphere became a concern lately in the production of PGM which are seen as metals to contribute to clean and renewable energy technology. SO_2 emissions are measured in terms of tons per day in the production process of PGM. This fact brought forth more considerations in reengineering process of handling and cleaning off-gas in plant operations. This paper further examined solutions provided in terms of processes and resources used to handle and clean off-gas as well as convert SO_2 to H_2SO_4 . Life cycle inventory tools were used for consideration and new conclusions drawn from results obtained which showed emissions from resources used as well.

Keywords

Platinum Group Metals, Plant Off-gas Cleaning, Inventory Assessment, Carbon Dioxide Equivalent Emissions

1. Introduction

The South African Bushveld complex is the largest economic potential of platinum group metals (PGM) resources ever discovered in the world estimated at about 80% of the world's reserves. Anglo American Platinum, the world's largest PGM producer, operates in the Western limbs of the Bushveld Complex exploiting the world's largest known igneous complex that extends over 65,000km² and reaches a depth of about 7km (Figure 1) (Mabiza, 2013).

In 2008, the overall restructuring operations of factories in the Anglo American Platinum was completed. The restructuring operations consisted of aligning newly owned mines with the new strategies put in place by the company to improve production, management, safety and environmental protection by reducing pollution and meet regulations. Sulphur dioxide (SO_2) emissions were identified the most noticed airborne pollution to be addressed in the recovery process of platinum group metals. Owing to its Precious Metals Refinery (PMR) and Base Metal Refining (BMR) units, the Anglo American Platinum shares ownership of some private mines, acquired by joint-venture agreements or other arrangements, the purchase of concentrates produced by private miners and enabling the company to maintain production up to 2,464 million ounces of PGM in 2009 compared 2,645 million ounces of production in 2008, an unwelcome occurrence in recent years (Anglo Platinum Limited, 2009). In addition, Anglo Platinum American also acquired a 17.5% stake in Johnson Matthey, a global leading producer of platinum electrocatalysts. Furthermore, through the first investment in its Platinum Group Metals Development Fund (PGMD Fund).

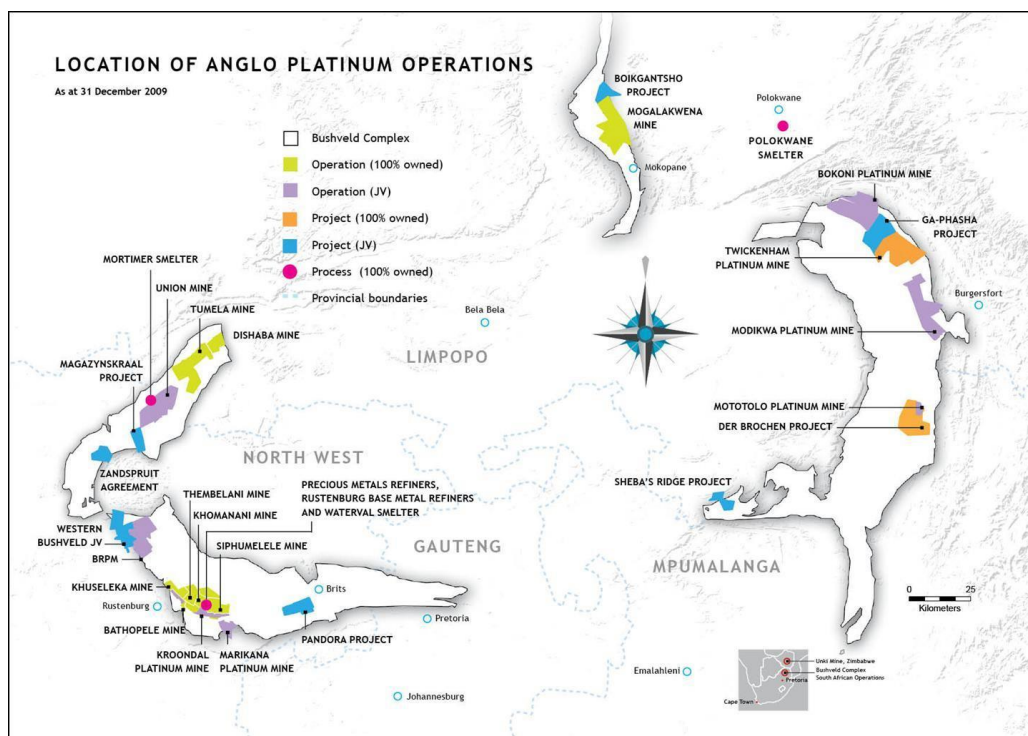


Figure 1: Location of Anglo Platinum operations in the Bushveld complex.
Source: (Groot and Pistorius, 2007)

2. Operational process for PGM recovery

2.1 Mining

An average concentration of PGM of about five grams (5g) can be found in one metric ton (1,000kg) of mined ore which can be sent directly to the Precious Metals Refinery (PMR) unit. The rest of the mined ore undergoes ore concentration operations. Precious metals are completely recovered from the mined ore (Jones, 2006).

2.2 Concentrator

The concentration unit is used mainly for the separation of valuable contents to rocks and sand. Ores undergo crushing, milling, and wet-screening to obtain pumpable slurry which bears the precious metals. Separation occurs in flotation cells where the reagents (chemicals) are added to aerate slugs carrying high-grade collected PGM (Anglo Platinum Limited, 2009). An approximate composition of a metric ton received at the ore concentration unit of Waterval is given in Table 1 below.

Table 1: Analysis of the concentrate at the Waterval ore concentration unit. Source: (Jones, 2006)

	Al ₂ O ₃ %	CaO%	Co%	Cr ₂ O ₃ %	Cu%	FeO%	MgO%	Ni%	S%	SiO ₂ %	PGM g/t	Total%
Anglo American Platinum Waterval	3.2	4.7	0.08	0.80	2.1	20	15	3.6	9	34	143	92

The composition of the above concentrate (Table 1), are required, precious metals (PGM plus gold) and metals (nickel (Ni), copper (Cu) and cobalt sulphate (CoSO₄)) (Anglo Platinum Limited, 2003).

2.3 Smelting

Smelting is a part of the process intended to recover precious metals from the concentrate slug by use of furnaces. A simplified smelter process flow schematic at the Waterval is given in Figure 2 below.

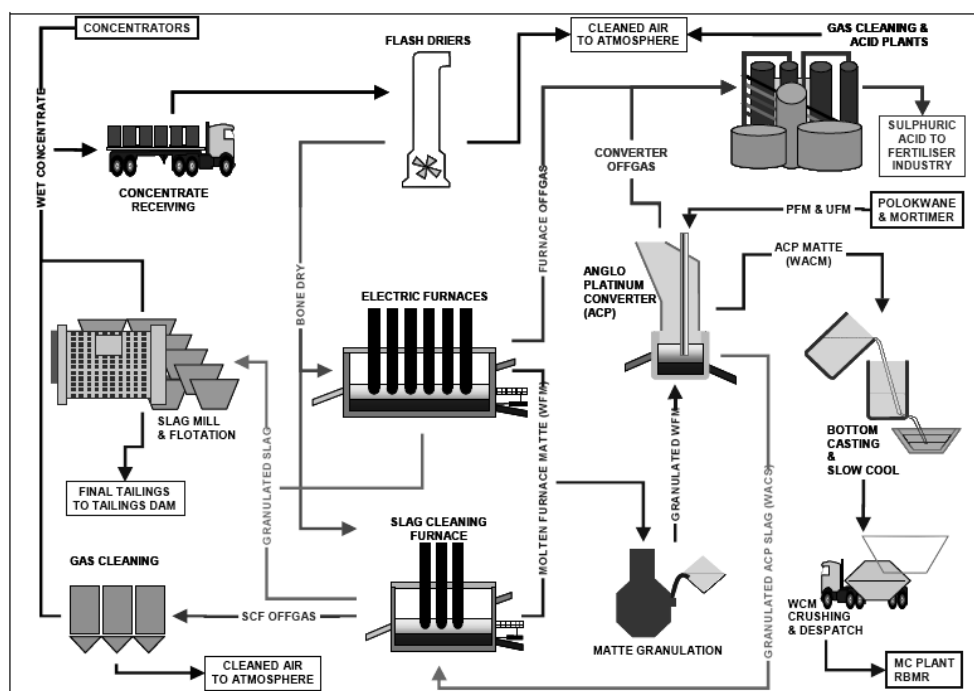


Figure 2: Simplified Smelter Process Flow Schematic at Waterval. Source: (Jacobs, 2006)

At an average temperature near to 1500°C, depending on the composition of the concentrate sulphide gangue mineral, a composition of silicate slag and oxide is separated from the inorganic sulphide matte and discarded. Matte then includes base and noble metals. According to Jacobs (2006), the analysis of the composition of furnace matte is as shown in Table 2, in which the iron (Fe) 41% and (S) 27%, both not needed, are still prevailing. In general this is the composition of the matte at this stage of the PGM recovery, in which 95% of the total of the slag is discarded. Smelters have a feed rate ranging from 25 to 54T / h.

Table 2: Furnace matte analysis at the Waterval Anglo platinum smelter. Source: (Jones, 2006)

	Co%	Cr %	Cu%	Fe%	Ni%	S%	PGMg/t	Total%
Anglo Platinum Waterval	0.5	0.5	9	41	17	27	640	95

Subsequently, at elevated temperatures the concentrate melts further and splits into two liquids phases; a lighter molten matte and slag rich in iron, having a density of about 2.7 to 3.3, is separated under the gravity from the molten matte, being denser, with a density of about 4.8 to 5.3 and rich in nickel and copper sulphides and in precious and base metals (Jones, 2006). The lighter molten matte is discarded and undergoes milling and cleaning of slag for possible recovery of PGM, and the molten matte is finally conveyed and discarded to the tailings dam (Figure 2).

2.4 The Furnace Matte Converting Process

The converter is designed to further separate the precious metals and base metals from the granulated matte. Because of its rich composition in iron (41%) and in Sulphur (27%) (Table 4), the granulated furnace matte undergoes a converting process in an attempt to completely remove Fe and S. This happens by blowing oxygen-enriched air through the top-submerged lance converter where the oxygen reacts with the furnace matte at high temperatures

ranging around 1300°C. The blown oxygen-enriched air can then oxidise Fe and S into iron oxide slag (FeO₂) and sulphur dioxide gas (SO₂) respectively. The iron in the matte can be cut down from 40% to around 3.5%. The converter can accommodate around 14,000t of furnace matte per month, an average of 459t per day, since 2006 (Jacobs, 2006). Due to considerable amounts of the oxygen-enriched air which are blown into the converter, a typical minimum production of 4% of a highly concentrated SO₂ composes the off-gases that leave the converter toward gas cleaning and acid plants (Jones, 2006). An estimated average of 14.4 tonnes of SO₂ emissions occurs daily at Waterval smelters and refineries and some fugitive SO₂ emissions from the mouth of smelters; these are emitted to the air from a stack (Anglo platinum, 2009).

2.5 Converter matte and slag analyses

The converter matte analysis in Table 3 shows the increase of concentration in base and precious metals when concentrations of Fe and S have been cut. After leaving the converter the matte can be processed by crushing and milling in order to separate base metals from the precious metals at the magnetic concentration plant (MCP). BMR is a process based on magnetic concentrate leaching and leaching electro-winning methods of producing Nickel, Copper and Cobalt sulphate; while PMR is based on dissolving and processing pure metal products, PGM and Gold.

Table 3: Converter matte analysis at the Waterval Anglo platinum converter Source: (Jones, 2006)

	Co %	Cu %	Fe %	Ni %	S %	PGM g/t	Total%
Anglo Platinum Waterval	0.5	26	2.9	47	21	2100	97

The following Table 4 shows the converter slag analysis. The converter slag is sent back to the furnace slag (auxiliary smelter) to attempt the recovery of any possible PGM concentration within the slag.

Table 4: Converter slag analysis at the Waterval Anglo platinum converter. Source: (Jones, 2006)

	Al ₂ O ₃ %	CaO%	Co%	Cr ₂ O ₃ %	Cu%	FeO%	MgO%	Ni%	S%	SiO ₂ %	Total%
Anglo Platinum Waterval	0.7	0.4	0.45	0.4	1.17	63	1.1	2.25	2.4	27	99

3. The Off-gas Handling Processes

3.1 The Cleaning of Off-gas and the Conversion of Highly Concentrated SO₂ at the Contact Plant

According to Jones (2006), the converter off-gases containing a highly concentrated SO₂ are subjected to a jet solid scrubbing and to a gas cleaning process at the gas cleaning section. The main acid-plant blower can thereafter draft the off-gases through a gas conditioning section where they are diluted with air or the off-gas from electric furnace to obtain a diluted gas containing 10% of SO₂. The diluted gas is first mixed with 65% Sulphuric acid (H₂SO₄) then with 92% H₂SO₄ to reduce the moisture content to less than 77mg/Am³. The conversion of the SO₂ in the diluted gas to Sulphur trioxide (SO₃) can be processed in the tower plant, at the contact plant. Through four passes consisted of vanadium pentoxide (V₂O₅) catalyst, SO₂ is converted to SO₃ in rates of 69% of SO₂ by the first pass in a hot heat exchange of 435°C. A total of 92.8% of SO₂ is converted by the second pass at a temperature raised to 503°C. An overall of 97.2% of SO₂:SO₃ conversion is attained by the third pass again cooled to 435°C. At the fourth pass, the overall conversion SO₂:SO₃ reaches approximately 99.91% and this happens at 447°C. The tail gas, cooled, goes to the final absorption tower where it is absorbed in 98.5% H₂SO₄ and passed through candle mist acid droplets and mist eliminators. Finally the residual tail gas is released to the atmosphere by means of a stack at less than 100ppm SO₂ concentration (Jones, 2006). The main reason for the SO₂-SO₃ transformation is the absolute avoidance of the air pollution by SO₂ pollution. SO₂-SO₃ transformation is a target to comply with regulations (Sichone, 2009). The tail gas released into the air is a composition with a low concentration in SO₂ of less than 100 parts per million (<100ppm); this means also only 100 molecules of SO₂ may be found in the composition of one million (1,000,000) molecules of the tail gas (Anglo Platinum, 2009). Due to the high rate of SO₂-SO₃ transformation, an important amount of H₂SO₄

can be collected at the acid plant proportionally to the capacity to handle the intermittent supply of the highly concentrated SO_2 . The SO_2 is then transformed into H_2SO_4 (Figure 4) (Rodney, 2004).

3.2 The Conversion of Weakly Concentrated SO_2

The weakly concentrated SO_2 is handled as well. This produces a weak sulphuric acid solution. The cleaning section continuously drafts electric furnace off-gas and off-gases across the plant which are collected at the pre-quench and post-quench towers to remove most of the solids that are carried away by the flow of gases. Oxygen from air and caustic soda are added to scrub out particulate matters in the off gas stream, casting them out into a tailings dam where they are all discarded variously as weak sulphuric acid, sodium salt, and slurry of dust. The cleaned off-gas is thereafter carried to the gas conditioning area where the removal of moisture occurs. The dried off-gas is directed into the denitration section whereby large amounts of nitrogen oxides (NO_x) are absorbed as well as SO_2 in part. Further absorption of NO_x occurs when the off-gas stream is passed through a balancing vessel $\text{NO}:\text{NO}_2$ in ratio 1:1. The off-gas with the remaining SO_2 is then ducted into the acid generation plant where it is absorbed to produce a strengthened (nitrosyl) sulphuric acid (HNO_3S). The off-gas is finally sent to the contact plant (Figure 4) to remove the residual NO_x and SO_2 gases where the tail gas results in less than 10 part per million of SO_2 (10ppm SO_2) and 100 ppm NO_x (Jones, 2006). In general, platinum mining companies are constrained to meet the compliance on SO_2 emissions in a limit rate of 25 tonnes per day enforced by the regulation; otherwise monetary penalties follow for non-compliance. Figure 3 following describes the trend of the Anglo Platinum Waterval smelter endeavours to aligning its SO_2 and NO_x emissions with the permitted rates since 2003-2010.

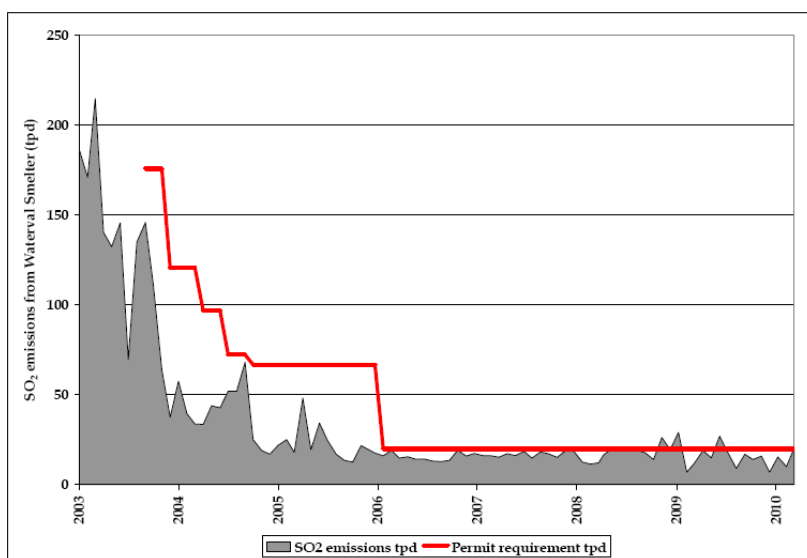


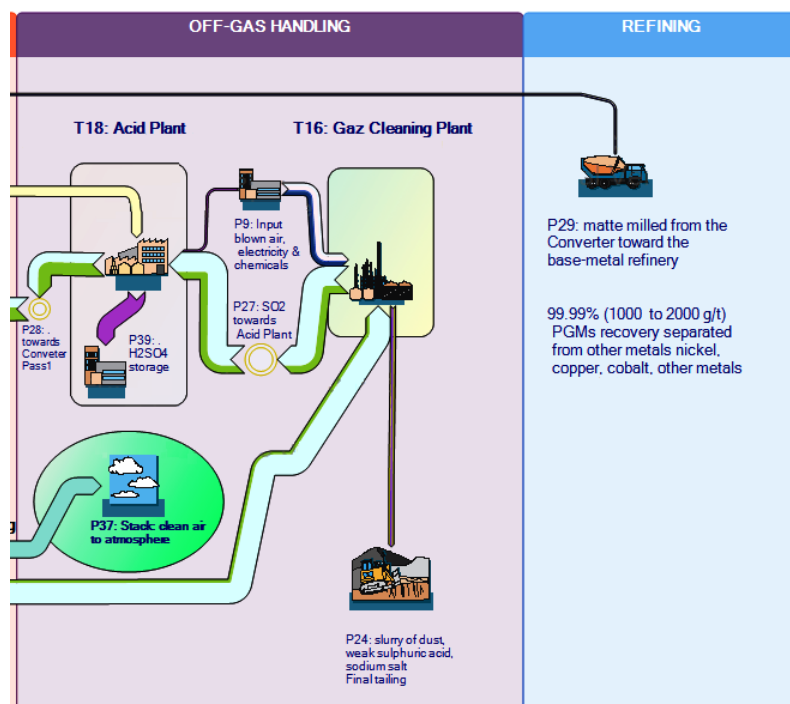
Figure 3: Decrease in SO_2 emissions at the Waterval Smelter; Source: (Hundermark et al., 2011)

Afterward the crushed converter matte is milled and sent in the magnetic concentration plant (MCP) whereby the precious metals fraction is separated magnetically. This is pressure leached to yield a solid final concentrate that is sent to a precious metals refinery (PMR). Base metal-rich non-magnetic solids and leach solution are processed further in the base metal refinery (BMR). PMR is based on the dissolution using hydrochloric acid and chlorine gas whereby PGM are sequentially separated and purified to yield platinum, palladium, iridium, ruthenium and gold. Osmium is precipitated as a salt. BMR is based on magnetic concentrate leaching and leaching electro-winning methods of producing nickel, copper and cobalt sulphate (Anglo American Platinum, 2011).

4. Inventory Assessment over off-gas handling process

The following Figure 4 portrays the process at the off-gas handling unit, the gas cleaning plant where off-gases are cleaned, the double absorption acid plant where SO_3 is absorbed by H_2SO_4 , the tailings dam where weak sulphuric acid solution, sodium salt and slurry of dust are discarded and the (exhaust) stack where the off-gas bearing weak SO_2 and NO_x is vented to the atmosphere.

4.1 Life Cycle Inventory of the flow-material in off-gas handling phase



[Figure 4: ACP gas cleaning process and acid plant processing at Waterval smelter. (Developed using Umberto software)]

4.2 Equivalent Carbon Dioxide

Table 5: Equivalent carbon dioxide to the off-gas handling process

Phase: OFF-GAS HANDLING: 511.52 kg CO ₂ -eq.			
cast iron, at plant [RER] (119.70 kg)	6.43E-14	kg CO ₂ -eq.	
copper, primary, from platinum group metal production [ZA] (49.11 kg)	1.74E-14	kg CO ₂ -eq.	
nickel, primary, from platinum group metal production [ZA] (52.67 kg)	3.58E-14	kg CO ₂ -eq.	
PGMs (1.12 kg)	1.90E-16	kg CO ₂ -eq.	
blown air (40.00 kg)	1.43E-15	kg CO ₂ -eq.	
sulfur dioxide gas, at platinum plant (0.14 kg)	2.71	kg CO ₂ -eq.	
magnesium oxide, at plant [RER] (7.62 kg)	-4.36E-15	kg CO ₂ -eq.	
cobalt, at plant [GLO] (2.36 kg)	6.33E-16	kg CO ₂ -eq.	
chromium oxide, flakes, at plant [RER] (144.32 kg)	-5.16E-15	kg CO ₂ -eq.	
sulfuric acid (249.86 kg)	107.80	kg CO ₂ -eq.	
fayalite (2FeO.SiO ₂) (178.01 kg)	-1.02E-13	kg CO ₂ -eq.	
Gas flow (2.339.22 kg)	401.01	kg CO ₂ -eq.	

The Table 5 above shows three constituents identified as source of emissions in the phase with quantified CO₂-eq emissions. Other constituents have no emissions related to this phase but rather involved as parts of the overall recovery process of PGM. In addition the three CO₂-eq emissions may be justified as emanating from energy-mix with 88% from coal burning power generation used by electric units in the phase and use of chemicals. The Table 5 also presents emissions over a typical composition of one tonne (1t) of ore mined and added resources. A total amount of equivalent carbon dioxide of about 511.52kgCO₂-eq is associated with the process. The masses displayed in the column "product" together with the designated constituents, are apparent weights which are in relation to the molecular masses of these constituents. They are the total masses of the constituents in the entire life cycle analysis of the assessed PGM recovery cradle, the mining, to gate, the off-gas handling process. The column "share", however depicts, by a length, the amount of CO₂-eq emissions emitted by each constituent in this phase (Table 5).

Conclusion

The cleaning of off-gas was analyzed with the use of life cycle inventory tools and these mainly revealed onsite or direct emissions when treating and converting polluting constituents and operational and indirect emissions due to the use of non-renewable energy-mix produced. If there may be admitted the gas effluxion effect insignificant, the three CO₂-eq emissions may be justified by the energy consumed by the units used and by the use of chemicals.

LCA in general strives to identify environmental challenges that are both overt and covert in a process based on constituents, their manipulation and methods used to reach objectives. In the case of off-gas handling process for PGM production, an emphasis should be also be put into bringing renewable and cleanly produced resources in the treatment of such as system. Energy and chemicals footprints should be rethought.

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