

Characterisation of SO₂ in off-gas at Zimplats smelter

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Abstract – Zimplats embarked on an off-gas sampling campaign in December 2009 to characterise the concentration of SO₂ in the off-gas from their 13 MW furnace. In excess of forty isokinetic samples (US EPA Method 8) were taken over seven days. The aim of the sampling campaign was to increase the understanding of factors that influence sulphur release from sulphide concentrates in an electric furnace. Specifically, detailed monitoring was conducted over various operating conditions to evaluate:

- The relationship between SO₂ and feed rate (*i.e.* furnace power)
- The relationship between SO₂ and ingress (*i.e.* furnace freeboard pressure)
- The impact of concentrate bed thickness on SO₂ (*i.e.* blacktop)
- The effect of events such as tapping and converter slag return on SO₂
- The desulphurization reactions that take place in the blacktop

A model was developed to predict the SO₂ content in furnace off-gas for a particular set of operating conditions. In order to evaluate the impact of random, uncorrelated changes in concentrate composition, ingress and power (feed rate) on the SO₂ content of the off-gas, a Monte Carlo approach was adopted whereby concentrate composition, power, and ingress were allowed to vary randomly around selected set-points.

The model is primarily based on the release of ‘labile’ sulphur from the partial thermal dissociation of sulphide minerals with an over-stoichiometric sulphur content (*e.g.*, Fe₇S₈ decomposition to FeS and S). The main findings of this work suggest that labile sulphur does not fully account for the measured SO₂ content of the off-gas, and that limited oxidation of sulphides during melting also contributes to the SO₂ content. Details of sulphide oxidation reactions in the furnace remain unclear, and it is currently not possible to provide a theoretical framework for the relationship between the extent of oxidation and variables such as temperature, gas composition, particle size, and residence time in the furnace black top. Through the use of the Monte Carlo model it was, however, possible to constrain the extent of sulphide oxidation to about 1%.

This work has shown in practice what was expected in concept, that SO₂ in off-gas is proportional to furnace power and ingress rate. The model that was developed consistently slightly under-predicts the quantity of SO₂ generated. It also highlights that more work is required to better understand the analytical methods used to analyse for SO₂ in off-gas.

INTRODUCTION

The applicability of a sulphur abatement technology is heavily dependent on accurately defining the SO₂ concentration in the off-gas. It is also important to understand the range of SO₂ to correctly evaluate operating costs of different technologies.

Hatch has developed a concentrate desulphurisation model to predict the concentration of SO₂ in furnace off-gas. The model is based on the release of labile sulphur from partial decomposition of sulphide minerals such as Fe₇S₈ and CuFeS₂ as the concentrate heats up in the blacktop. Elemental sulphur that is released reacts with oxygen to form SO₂, which is diluted by ingress air. Qualitatively, the model predicts that, for a particular concentrate, the SO₂ content of the furnace off-gas will be proportional to the feed rate (or furnace power) and inversely proportional to the rate of air ingress. It is important to note that the amount of labile sulphur released by the concentrate depends on the sulphide mineralogy. Therefore, in principle, it is possible that two concentrates with the same bulk composition could release completely different amounts of labile sulphur. Measured off-gas SO₂ levels from one furnace can therefore not be extrapolated to another furnace operating with a different concentrate, even if concentrate compositions are very similar.

There was an obvious need to correlate the concentrate desulphurisation model against actual plant measurements under controlled process conditions. To this end, a furnace off-gas sampling campaign was undertaken at Zimplats. The campaign was primarily designed to test the impact of furnace power (feed rate) and freeboard pressure (ingress) on the SO₂ content of the off-gas, and to compare the measured gas composition against model predictions. Some other process variables that were found to impact the off-gas composition, but are not included in the model, were also documented. These variables include concentrate bed depth, furnace events such as tapping, and the return of converter slag.

MEASUREMENTS AND MODELLING

Sampling Method

Three sampling ports were installed on the off-gas duct on the slipping floor (Figure 1). The sampling location was selected on the basis of proximity to the furnace roof (to minimize air leakage into the duct upstream of the sampling location) and gas flow behaviour (for isokinetic flow, the sampling location should be ~8 duct-diameters downstream from any inflection point in the duct, and 2 duct-diameters upstream of any inflection point²).



Figure 1: Location of gas sampling ports on the slipping floor.

Furnace operating conditions were monitored and the following parameters were recorded:

- Furnace bath levels
- Slag and matte temperatures
- Roof temperature
- Freeboard pressure
- Furnace throughput (feed rate)
- Furnace power
- Furnace events (*e.g.* slag return)

The industry-accepted US EPA Method 8 was used to measure the average concentrations of SO₂ and H₂SO₄ in furnace off-gas.

In addition to the US EPA Method 8 samples, a calibrated TESTO 350S flue gas analyser was used to continuously monitor the concentration of SO₂¹. Continuous temperature, pressure, and gas velocity trends were also logged.

Furnace conditions

The furnace process conditions during the sampling campaign are shown in Tables I and II.

Table I: Ranges of furnace process conditions during sampling campaign

Parameter	Value
Furnace power	7 – 13 MW
Feed rates	3 – 26 t/h

Table II: Average concentrate analysis during sampling campaign

Ni (%)	Cu (%)	Co (%)	Fe (%)	S (%)	CaO (%)	MgO (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	Cr ₂ O ₃ (%)
3.730	2.674	0.116	15.157	7.185	2.150	20.979	1.418	44.823	0.292

¹ The instrument was calibrated before the sampling campaign. The calibration was again checked on completion of the work. Drift was found to be negligible.

Sampling and Analytical Procedures

Following two trial runs, it was realised that the high dust loading at the sampling location caused blinding of the filters, and therefore sampling conditions were not isokinetic over a one-hour period. The use of a water trap was considered, but discarded after a trial run returned an anomalously low off-gas SO₂ reading, suggesting that some SO₂ is absorbed in the water. It was subsequently decided to retain the original sampling train but to reduce sampling times to 30 minutes to mitigate the high dust levels. A reduction in sampling time is generally accepted during SO₂ sampling of batch processes, and is not considered to be a serious deviation from the Method 8 sampling procedure. Samples were analysed for SO₂ on site using a titration method, as per the EPA Method¹. Subsequently, all the samples collected were also analysed by ion chromatography (IC).

The agreement between the titration and IC results was generally poor, despite the fact that both data sets support the same general trend of higher values at higher furnace powers. There is a clear bias of the IC results to higher SO₂ levels with some of the IC results improbably high. The IC results are also less precise. The discrepancy between the IC- and titration-results was queried with SGS-Ecoserv and also with an EPA Method 8 specialist, Mr Gary McAlister. It transpired that:

- The barium perchlorate/thorin titration has a number of potential problems. It only really works well for very 'clean' samples. Metal cations cause a nonspecific interference because they can complex with the thorin, as does barium, to alter the colour of the solution, making the colour change at the endpoint of the titration difficult to see.
- The pH of the solution is important, as a sharp colour change is only obtained in solutions that have a very acidic pH, with a preferred range of 2.5 to 4.0. In this regard, it should be noted that the sample solutions contain an organic component (isopropyl alcohol) and the pH of the samples is unknown.
- Anions, especially fluorine and phosphate, also cause interference.
- The IC method is not susceptible to interferences, but, because of the high SO₂ level in the samples, requires a roughly 2 000-fold dilution. The very high dilutions result in a gross error estimated (by SGS) of about 20%, relative.

The Method 8 solutions are unlikely to be 'clean' in the context of the comments from Mr McAlister. In addition to isopropyl alcohol, metal cations (notably zinc, lead, and arsenic) and anions (such as chloride and fluoride) are likely to be present in trace amounts, and it is recognised that interferences may be responsible for an unquantified, systematic bias in the titration results.

A 20% dilution error explains the relatively poor precision of the IC results, but does not explain the tendency of the IC readings to be offset to higher SO₂ values. While investigating the data integrity, it was noted that there is a strong correlation between the IC readings and the dust loading of the gas. Dust,

which is collected on a heated filter upstream of the SO₂ scrubbing solutions, should not interfere with SO₂ collection, and the observed correlation, which may point to sample collection problems at high dust loads, remains unexplained.

The TESTO electrochemical sensor that was used for continuous, on-line analysis of the SO₂ content of the off-gas is not vulnerable to gas purity, although the analyser has to be regularly purged during use to avoid desensitising the probe. These interruptions are reflected as gaps in the SO₂ data trends (Figure 3). The instrument was calibrated against a standard gas before use. After the measurement campaign, the calibration was again checked to monitor instrument drift during use. Drift was found to be insignificant. The main problem with the TESTO flue gas analyser is that the process gas requires significant dilution (approximately 10-fold) for the SO₂ concentration to fall within the analytical range of the instrument. Gas dilution obviously affects the precision of the data obtained from the TESTO analyser.

Results

Figure 2 illustrates the impact of furnace power on the SO₂ in off-gas (samples analysed by titration). Individual tests were run at various dilution rates resulting in a significant data spread, hence the use of bands to illustrate the distribution of data points. As expected, operation at higher power generally results in higher SO₂ in off-gas, but it is interesting to note that the bands overlap, suggesting that, between 7.5 and 11 MW, furnace power has a smaller effect on SO₂ than ingress has.

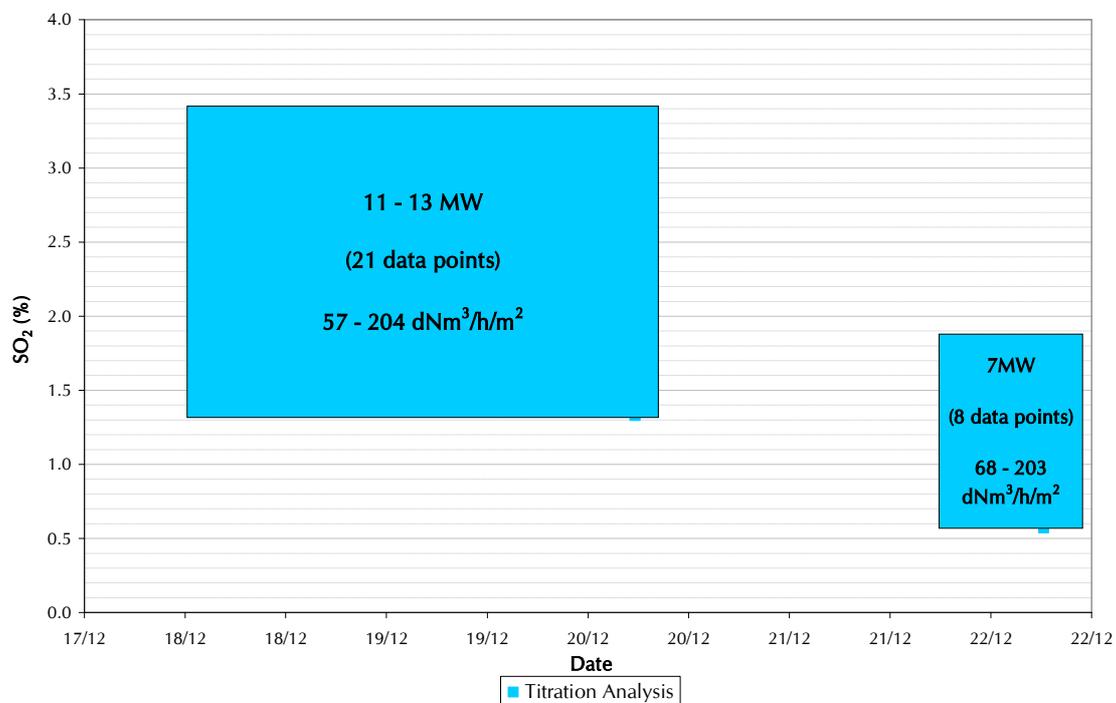


Figure 2: Overview of the Method 8 (titration) data for operation at 11-13 MW (18, 19, and 20 December) and 7 MW (22 December)

Figure 3 illustrates the significant impact of ingress on the SO₂ concentration. The freeboard pressure set point was deliberately manipulated to increase the ingress air just after 11am on 22 December. The gas velocity (converted to ingress rate) increased from approximately 60 Nm³/h/m² to about 220 Nm³/h/m², and, as expected, both the gas temperature and SO₂ concentration decreased (temperature from about 320°C to 230°C, and SO₂ from about 1.7% to 0.7%).

The data trends for 22 December show an interesting pattern that was consistently observed during the sampling campaign; the return of converter slag to the furnace resulted in sharp, short-lived spikes in temperature and SO₂. Apart from ingress-related variations, these spikes are the main source of variation in furnace gas composition.

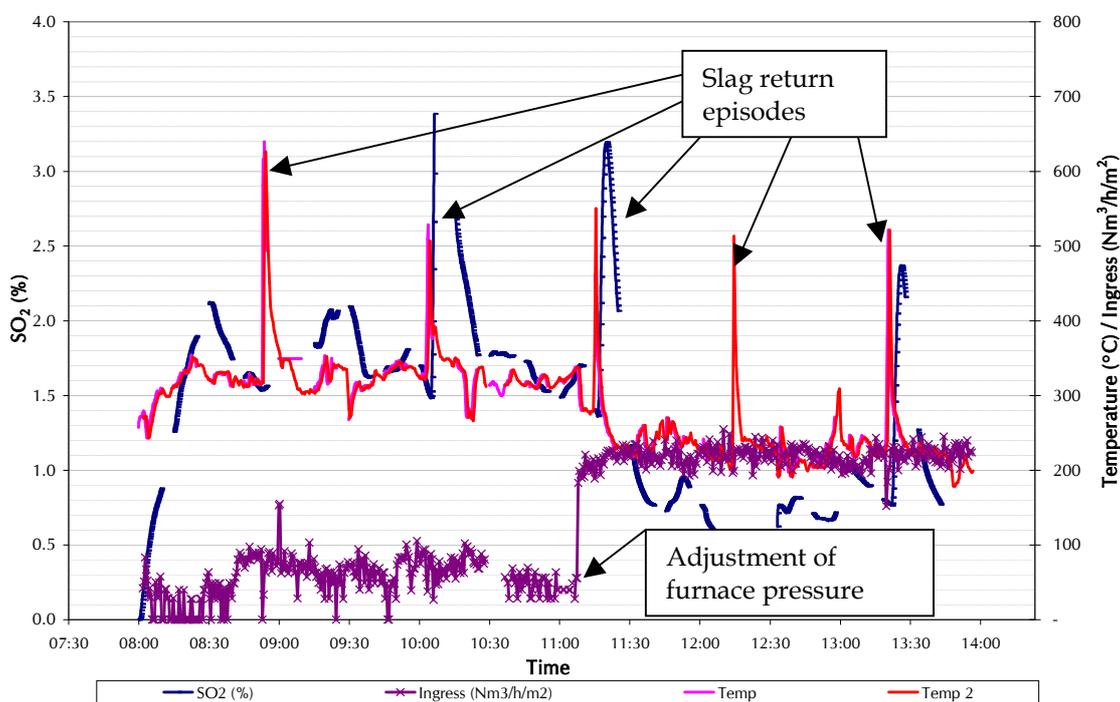


Figure 3: Furnace data trends for 22 December 2009. SO₂ data are from the TESTO flue gas analyser. Spikes in freeboard temperature and SO₂ are caused by the return of converter slag to the furnace.

Within the resolution of the data that were collected during the sampling period, there does not seem to be a correlation between the thickness of the blacktop and either off-gas temperature or SO₂ content. That SO₂ does not strongly correlate with the thickness of the blacktop implies that sulphur generation is not kinetically limited. If kinetic factors controlled the release of sulphur at temperatures below the liquidus temperature of the concentrate, lower SO₂ values would be obtained with a thinner blacktop (because of a shorter residence time of the concentrate in the blacktop). Since the release of SO₂ from the blacktop is not kinetically controlled, it is unlikely that desulphurization will significantly depend on furnace geometry (round versus rectangular).

SO₂ modelling

Hatch uses a model that predicts the SO₂ in the off-gas based on the following inputs:

- The sulphide mineralogy of the concentrate, calculated from the sulphur content
- Feed rate, which is related to furnace power through the SEC. For the Zimplats campaign, a feed rate of 16.2 t/h was used.
- Ingress air rate. The %SO₂ in off-gas is expected to be related to ingress by a simple 'dilution' equation of the form %SO₂ = Vol SO₂ / Ingress.

Bulk chemical analysis of the concentrate is used to calculate the modal sulphide mineralogy. Nickel, copper, and cobalt are assigned to the minerals pentlandite (Ni₉Fe₈S₁₅), chalcopyrite (CuFeS₂), and covellite (CoS), respectively. The remaining sulphur is distributed between the sulphide minerals pyrrhotite (Fe₇S₈) and pyrite (FeS₂). The ratio of pyrrhotite-to-pyrite is a fundamental property of each particular concentrate and must be measured. For concentrates from the Bushveld Complex and Great Dyke, the predominant sulphide mineral is typically pyrrhotite, and without introducing significant error it was assumed that 80% of the sulphur in iron sulphides is present in pyrrhotite.

During heating of the concentrate in the blacktop, labile sulphur is generated by the following decomposition reactions:



Sulphur released by Reactions 1 to 4 oxidises to form SO₂, which is diluted by ingress air. Assuming there is no further desulphurisation, metal sulphides formed by Reactions 1 to 4 (Ni₃S₂, Cu₂S, and FeS) collect as matte. These reactions can, therefore, be used to predict the matte composition, which, in turn, can be benchmarked against the actual composition. The following became clear when the model output was compared to actual matte compositions (Table 1):

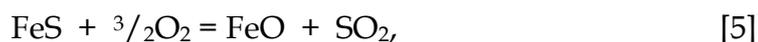
- The composition of furnace matte is not just a weighted average of the sulphide minerals in the concentrate. Specifically, the sulphur content of the matte is much lower than the weighted average value.
- Matte composition predicted on the basis of labile sulphur removal through reactions 1 to 4 agrees more closely with the measured composition, but still over-predicts the sulphur content remaining in the matte.

- Labile sulphur accounts for most of the difference between the sulphur content of the matte and the weighted average of the sulphide minerals in the concentrate. Labile sulphur, therefore, provides a credible, if slightly under-predicted, estimate of SO₂ that will be generated in the blacktop.
- Actual matte fall will be slightly lower than the value predicted from the labile model.

Table II: Actual and predicted matte compositions from Impala and Zimplats, mass %

	Ni	Cu	Fe	S
Zimplats: 08/09/2008 - 11/09/2008				
Average furnace matte composition	15.6	10.4	41.9	31.4
Predicted matte composition assuming release of labile sulphur	14.4	9.6	43.2	32.6
Weighted average of sulphide minerals in the concentrate	13.5	9.0	40.9	36.5

The lower sulphur content of matte relative to the value predicted from the labile model is readily explained by oxidation reactions that liberate sulphur in the blacktop. Oxidation reactions may directly release sulphur; *e.g.*,



or via the formation of intermediate sulphate phases:



In the absence of reductant, metal sulphates decompose to form oxides, and release SO₂ when heated above the stability temperature of the sulphates, which is typically in the range of 400 - 600°C.

In order to evaluate the impact of random, uncorrelated changes in concentrate composition, ingress, and power (feed rate) on the modelled SO₂ content of the off-gas, a Monte Carlo approach was adopted whereby concentrate composition, power, and ingress were allowed to vary randomly around selected set-points.

Model Results

Figure 4 compares the distribution of the sampling results and the results from the Monte Carlo analysis. It is clear that they correlate well, with the model slightly under-predicting SO₂. When the model was adjusted to incorporate 1% oxidation in the freeboard (Figure 5), the results correlated more strongly.

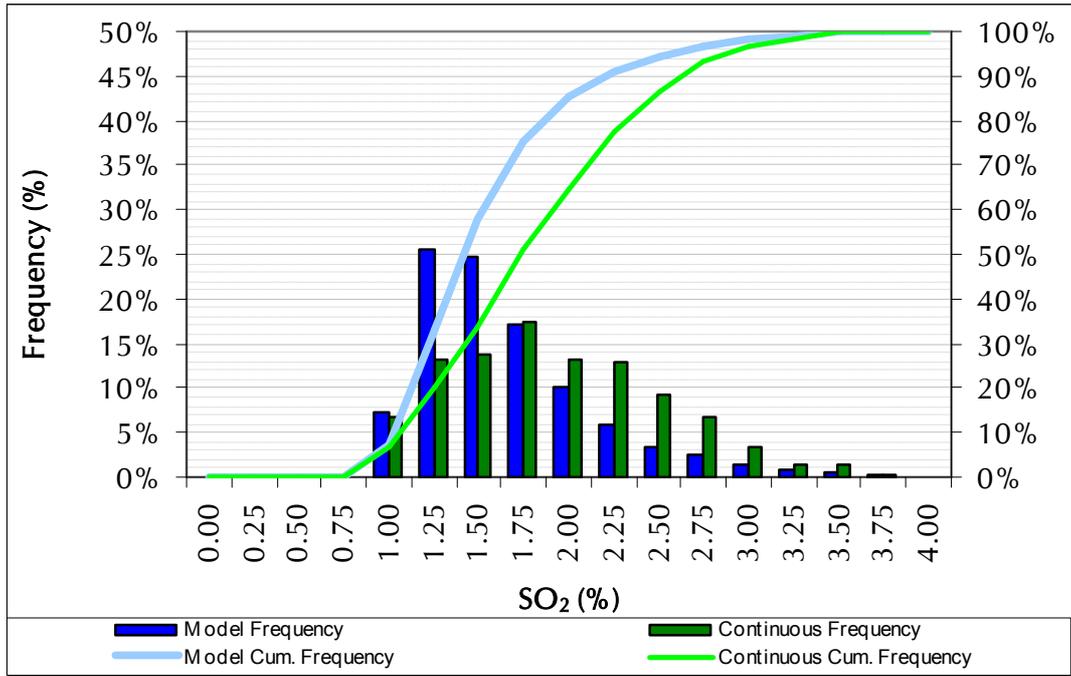


Figure 4: Predicted variation in SO₂ for a 13 MW furnace, in response to variable model parameters. The distribution of SO₂ measurements extracted from the continuous TESTO data trends is included for comparison.

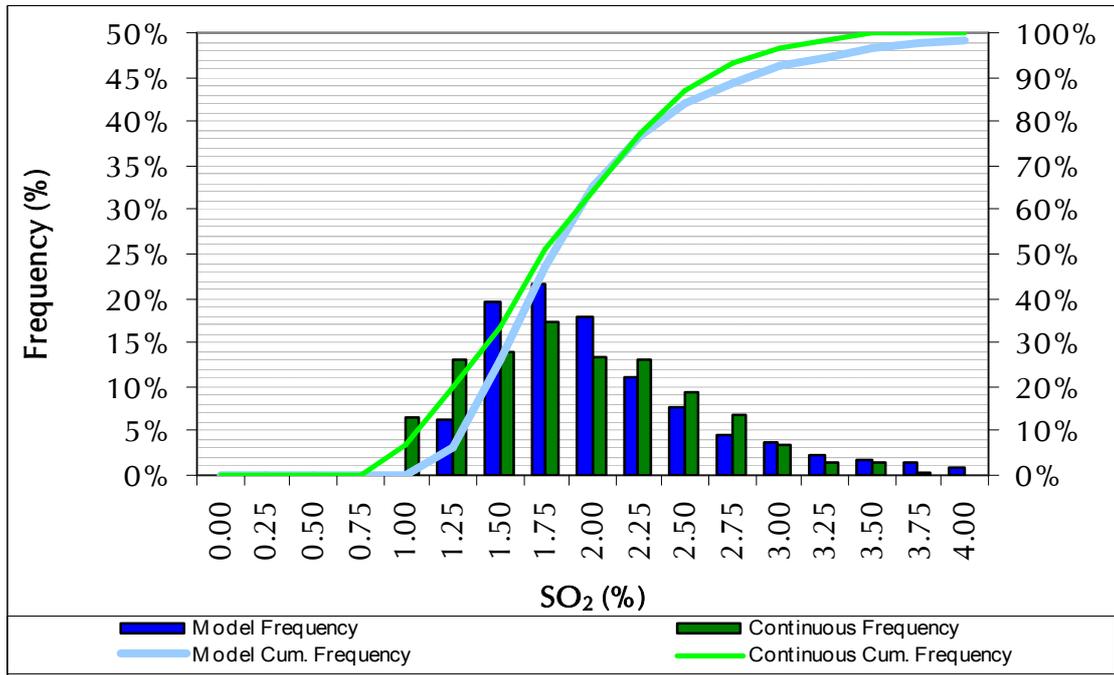


Figure 5: Predicted SO₂ for the 13 MW furnace at a matte fall of 99%, compared with the continuous measurements obtained with the TESTO analyser. The model is based on the liberation of labile sulphur (Reactions 1 - 4) and the oxidation of a further 1% of the sulphide minerals that are formed when labile sulphur is generated.

As expected, the labile model under-predicts SO₂ in the furnace off-gas (because the labile model over-predicts sulphur in furnace matte). In addition, the following should be noted (Figure 6):

- With increasing ingress rate, the effect of a change in ingress rate on the SO₂ content of the gas decreases, and the gas composition is more stable. Conversely, at low ingress rates, gas composition is more sensitive to changes in the ingress rate, and gas composition is expected to be less stable.
- At a constant ingress rate, the labile model predicts a stronger relationship with power (feed rate) than what is observed. In part, this may be attributed to the oxidation of sulphide minerals that also release SO₂ into the furnace off-gas.

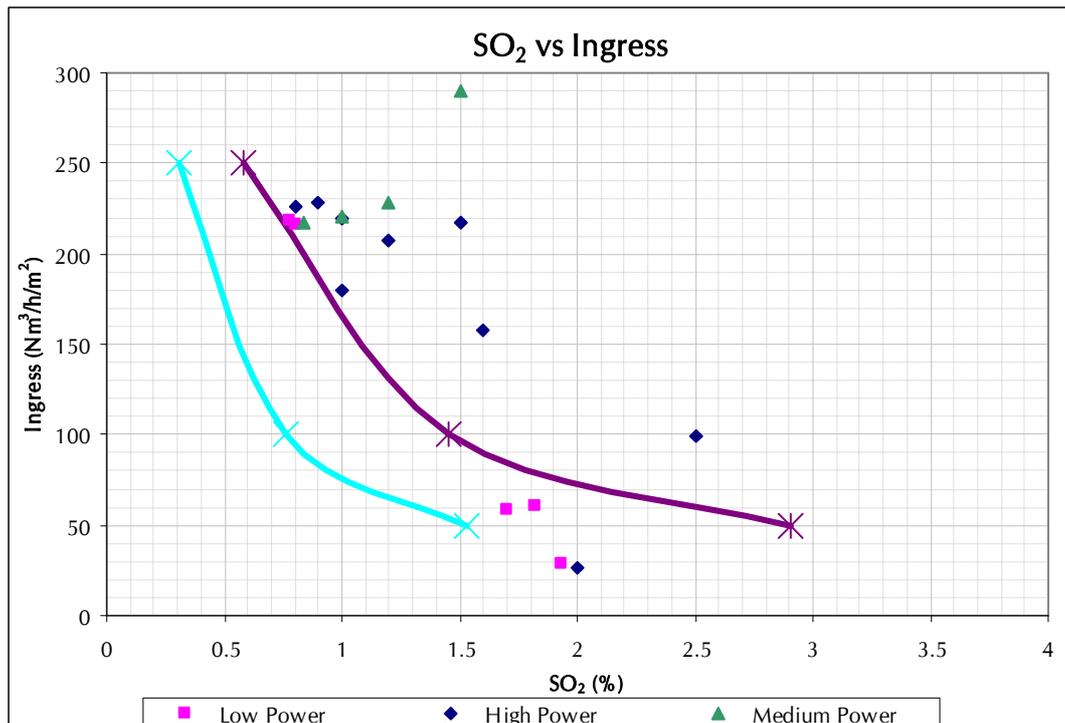


Figure 6: Predicted SO₂ at 7 MW (turquoise) and 12 MW (purple), compared with the measurements obtained from the TESTO in-stack emission analyser. The model consistently under-predicts measured values, especially at low power. Because of analytical uncertainties in the measurement of SO₂, the offset may be bigger than suggested by these relationships.

CONCLUSIONS

Measuring SO₂ in furnace off-gas is not a trivial exercise, and there are several interferences that can be expected. Sampling confirms that expected relationships between SO₂ in off-gas and ingress rate (freeboard pressure) and feed rate (power) do apply. A single unit value for SO₂ in off-gas is not a realistic representation of the process conditions, but, rather, an operating range should be developed.

ACKNOWLEDGEMENTS

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REFERENCES

1. United States Environmental Protection Agency, *Method 8 – Determination of Sulphuric acid and Sulphur Dioxide Emissions from Stationary Sources*, USA, 1996.
 2. United States Environmental Protection Agency, *Method 2 – Determination of Stack Gas Velocity and Volumetric Flow Rate*, USA, 1996.
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Johan is a Process Consultant with more than 20 years experience in applied mineralogy, metallurgical thermochemistry, process metallurgy, and management. He has in-depth knowledge on aspects such as matte smelting of chromium-bearing PGM concentrates, the recovery of PGMs from secondary sources, converting of PGM-bearing alloys.



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Rose is a chemical engineer with four years of experience in process development, technology selection, design and engineering of off-gas handling systems and related equipment. Rose has a good understanding of the South African regulations for air emissions.
