

FLUE GAS CONDITIONING – SO₃ INJECTION RATES FOR SOUTH AFRICAN COAL ASHES

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ABSTRACT

Flue gas conditioning at some Eskom power stations has required lower SO₃ injection rates than those predicted by models or FGC vendor experience. The required injection rates were about a third of predicted, which was an unexplained anomaly. The paper offers an explanation and proposes a method for determining whether a coal ash will behave “conventionally” with SO₃ FGC or will require a lower than expected injection rate.

1. INTRODUCTION

At many of Eskom's coal-fired power stations, fly ash (dust) is filtered from the flue gases with electrostatic precipitators (ESPs).

To extend South Africa's coal reserves; low-grade coals with high ash contents are burned for power generation. Because these coals have low sulphur contents, less sulphur is emitted from the chimneys, but larger quantities of difficult to collect fly ash are produced.

As part of Eskom's emission enhancement programme, flue gas conditioning (FGC), using sulphur trioxide (SO_3), is presently installed at over 50% (16 974 MWe) of installed generating capacity. This technology has proved cost effective in reducing emissions from South African low sulphur coals. It is probable that Eskom is the biggest single user of FGC in the world.

In most cases, the SO_3 FGC injection rates were in the 20 to 30 ppmv (parts per million volumetric) range, which agreed either with model predictions or with industry experience. However, for both Duvha and Kendal Power Stations, the measured optimum SO_3 injection rates were significantly less than predicted, or expected. Until recent investigations and discoveries by Eskom Technology Services International (TSI), Duvha and Kendal were unexplained anomalies.

1.1 Ash Resistivity

The electrical resistivity of a fly ash, deposited on the collecting electrodes (plates) of an electrostatic precipitator (ESP) in good mechanical condition, has a major influence on ESP performance.

The ideal range of resistivities for optimum ESP performance, at temperatures below, 180°C is considered to be from 1×10^{10} to 3×10^{10} ohm.cm. At up to 5×10^{11} ohm.cm, good ESP performance can still be expected, with a rapid reduction at higher resistivities.

To summarise:

10^7 ohm.cm	particles discharge and re-entrain back into gas stream
1×10^{10} to 3×10^{10} ohm.cm	ideal range for ESP operation
10^{11} ohm.cm	back ionisation starts
10^{12} ohm.cm	back ionisation stable

Most of the fly ashes encountered within Eskom are in the 10^{13} ohm.cm range and should be referred to as "extreme resistivity" ash instead of "high resistivity", even though this term is not commonly used.

1.2 Flue gas conditioning with SO_3

The electrical resistivity of a fly ash depends upon its chemical composition and the composition of the flue gas in which the ash particles are suspended. The composition of the ash determines its volume resistivity, whereas the composition of matter deposited on the particle surfaces, such as moisture and acid, determine the surface resistivity. The effective resistivity is a combination of volume and surface resistivities. At temperatures below 180°C , surface resistivity is dominant.

The presence of sulphur compounds greatly influences the resistivity of fly ash. High sulphur coals produce fly ashes that are more readily collected in an ESP than ashes from low sulphur coals. The sulphur in coal converts on combustion to sulphur dioxide (SO_2), a small proportion of which converts to SO_3 . The proportion of SO_2 converted varies from boiler to boiler, ranging from 0.1% to 0.4%. The SO_3 combines with the moisture in the flue gas and forms H_2SO_4 , which deposits on the particle surfaces and forms an electrically conductive layer. Most South African power generating coals have low sulphur contents (<1.5%) and do

not produce enough SO₃. Flue gas conditioning (FGC) with sulphur trioxide (SO₃) supplements the naturally occurring SO₃ to reduce the resistivity into the optimum range.

In permanent SO₃ FGC installations, elemental sulphur is burnt to form SO₂, which is then catalytically converted to SO₃. A hot air and SO₃ gas mixture is fed into a manifold and injected into the flue gas stream, through nozzles distributed along injection lances. This is usually done at a point close to the air-heater flue gas outlet, to give the SO₃ maximum residence time for it to treat the fly ash before entering the ESP.

2. SO₃ FGC EXPERIENCE IN ESKOM

2.1 SO₃ FGC Plant

SO₃ FGC tests and trials have been conducted at Arnot, Camden, Duvha, Grootvlei, Hendrina, Kriel and Matimba Power Stations [6.1 to 6.9 & 6.13]. Permanent SO₃ FGC plants are installed at Hendrina, Kendal, Kriel, Matla, Duvha and Lethabo Power Stations [6.10 to 6.14].

2.2 SO₃ FGC Injection Rates

In the majority of cases, the SO₃ injection rates were in the 20 to 30 ppmv (parts per million volumetric) range. However, for both Duvha and Kendal, the measured optimum SO₃ injection rates were significantly less than those predicted with the Wahlco SO₃ injection rate computer model (Table 1), or with SO₃ FGC industry expectations. [6.15 to 6.17]

TABLE 1
Optimum SO₃ FGC Injection Rates

Station	Predicted (Wahlco) ppmv SO ₃	Measured (TSI) ppmv SO ₃	Ratio (Averages) TSI/Wahlco ratio	Predicted (Acid/Base) ppmv SO ₃
Arnot	15 to 21	22	1.2	9 to 14
Matimba	43 to 51	35 to 45	0.9	12 to 18
Duvha	33	13	0.4	11 to 16
Kendal	27.5	7.5	0.3	11 to 16

Because they were amongst the last to be tested, Arnot and Matimba were selected to represent "conventional" SO₃ injection rates. Duvha and Kendal were, at the time of the investigations, the unexplained anomalies.

Later, a different SO₃ injection rate prediction model, using the Acid/Base ratio, was used to look at the data. Although it gave a better prediction for Duvha and Kendal, it was significantly out for Arnot, Matimba, and the others.

2.3 Reaction of Fly Ash to SO₃

In 1997, Duvha fly ash was compared to that of Majuba, because Duvha experienced acid degradation of the bag fabric in the baghouses of Units 1 to 3, whereas Majuba did not. It was found that no SO₃ (i.e. H₂SO₄) reacted with the calcium in the Duvha fly ash and the acid was not neutralised. The calcium in the ash was locked into a mineral, or into a form of amorphous glass, that could not react with the SO₃ in the flue gas. The acid accumulated in the dust cake on the bags and attacked the bag fabric [6.18]. Whether the calcium in the fly ash can react with SO₃, or not, appears to be dependent on a combination of factors, such as coal and ash composition, as well as furnace and burners types, and combustion process.

The research into the mechanism of premature filter bag degradation, for Duvha Units 1 to 3, provided a clue to explain why the Duvha and Kendal ESPs required lower SO₃ FGC injection rates. [6.18 to 6.20] Because little, or none, of the SO₃ reacted with the calcium, most of the

SO₃ was available to form a conductive layer on the ash surfaces. As a result, far less SO₃ was required to effectively condition the fly ash.

2.4 Investigation

At the time of the above realisation [2.3], Lethabo was considering the installation of SO₃ FGC. A project was initiated to substantiate the theory, so that the Lethabo fly ash could be characterised as needing a “conventional” or “reduced” amount of SO₃ FGC.

The identification, of whether the calcium in an ash was locked into a mineral, or into a form of amorphous glass, that could not react with the SO₃ in the flue gas, required sophisticated analyses using a scanning electron microscope (SEM). Since the reactivity of a fly ash to SO₃ was of interest, and not what is was due to, a simpler method was sought to identify and quantify the reactivity of a fly ash.

The stations selected for the investigation, together with reasons, are shown in Table 2. In addition, Duvha and Arnot have both fabric filters and ESPs. For economy, data obtained for other investigations, was used as much as possible.

TABLE 2
Stations Selected for Investigation

Station	Filter type	Interest in SO ₃ FGC?	Baghouse chemistry data?	Acid attack on filter fabric?	Conventional SO ₃ FGC rate?	Lower SO ₃ FGC rate?
Lethabo	ESP	Yes				
Kendal	ESP					Yes
Duvha	FF & ESP		Yes	Yes		Yes
Arnot	FF & ESP			No	Yes	
Majuba	FF		Yes	No		

3. ANALYSES

The following analyses and investigations were conducted.

3.1 Coal and Ash Analyses

3.1.1 Coal Analyses

Coals were analysed for proximate and ultimate composition, as well as heat value.

3.1.2 Ash Elemental Analyses

Ash elemental compositions were determined with x-ray fluorescence (XRF) spectroscopy. Since, XRF is not suitable for sodium (Na) and lithium (Li), atomic absorption (AA) and/or induction coupled plasma (ICP) spectroscopy was used for these two elements. With elemental analyses, the elements are reported as stable oxides, which do not necessarily reflect the compounds or minerals that do occur. For example, sulphur is reported as SO₃ (a gas), but occurs as a sulphate.

3.1.3 Ash Mineralogical Analyses

The mineralogical composition of the ash was analysed using x-ray diffraction (XRD) spectroscopy.

The resolution of the XRD, at the time of the investigations, was;

>10% to 100%	Major Phase
>1% or 2% to <10%	Minor Phase
<1% or 2%	Not Detected

3.1.4 Ash Alkalinity

The alkalinity of the ash and its reactivity to sulphuric acid (H_2SO_4) were determined to indicate the available calcium (Ca), in or on the ash, which is capable of neutralizing SO_3 in flue gas.

A ratio of 1:2.5 ash to water slurry was prepared and well mixed for 20 minutes. The ash was allowed to settle and the total alkalinity of the supernate was determined using 0.02N HNO_3 . In addition, 10 ml of the supernate was neutralized to pH 7.0 using 0.02N H_2SO_4 .

3.1.5 Computer Modelling SO_3 Injection Rate

Using a proprietary in-house computer model, developed by Lee Coe [9.15 to 9.17], Wahloco determined predicted SO_3 FGC injection rates.

The model also predicts the flue temperature at which SO_3 ceases to be effective for a particular ash.

For the example in Figure 1, the injection rate at $140^\circ C$ would be 37 ppmv. The start of the "knee" indicates that SO_3 FGC will rapidly cease to be an effective means of emission reduction at temperatures in excess of $170^\circ C$ for that particular ash.

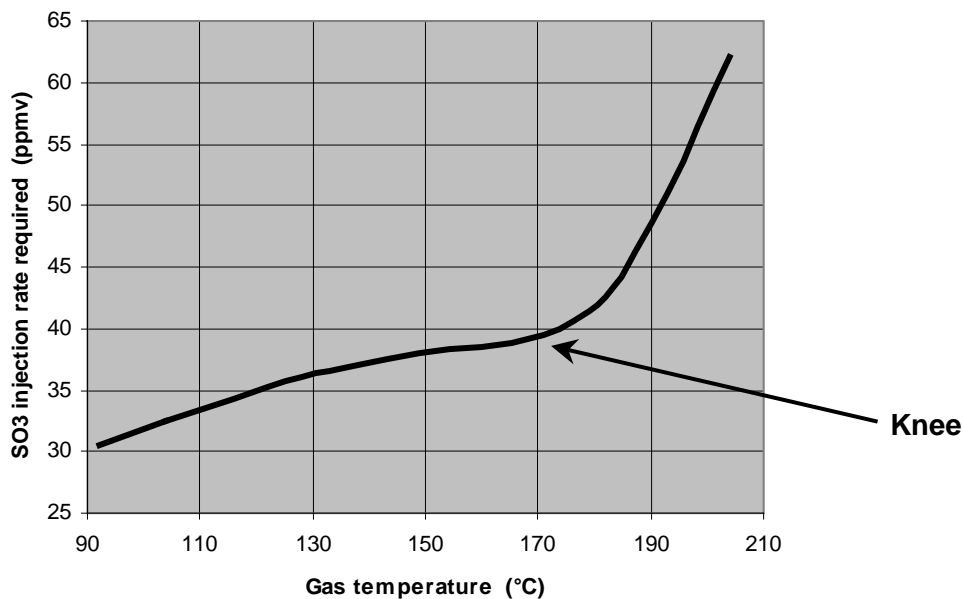


FIGURE 1
Typical Relationship Between SO_3 Injection and Flue Gas Temperature

4. RESULTS & DISCUSSIONS

4.1 Coal Analyses

TABLE 2
Coal Analyses

STATION		Lethabo	Kendal	Duvha	Arnot	Majuba
Date		24-Apr-98	Apr-97	Feb-97	Jul - Aug-97	No data
MOISTURE						
Surface moisture	%	4.7	2.5	2.4	3.8	
Inherent moisture	%	5.6	3.7	2.7	3.2	
Total moisture	%	10.3	6.2	5.1	7.0	
PROXIMATE						
Inherent moisture	%	5.6	3.7	2.8	3.2	
Ash	%	36.5	27.6	23.0	22.7	
Volatile matter	%	21.1	22.6	20.8	21.9	
Fixed carbon (by difference)	%	36.8	46.1	53.4	51.9	
ULTIMATE						
Inherent moisture	%	5.6	3.7	2.8	3.2	
Ash	%	36.5	27.6	23.0	22.7	
Carbon	%	43.45	54.38	62.44	59.36	
Hydrogen	%	2.2	3.2	3.4	3.1	
Nitrogen	%	0.98	1.18	1.44	1.23	
Sulphur (total)	%	0.49	0.90	0.61	0.56	
Carbonate (as CO ₂)	%	1.95	1.80	0.36	1.62	
Oxygen (by difference)	%	8.83	7.35	5.99	7.97	
Gross calorific value	MJ/kg	16.22	21.05	24.10	22.49	

4.2 Ash Elemental Analyses

The elemental analyses are given in Table 4. The analyses were with XRF, but if shaded, Na and Li were analysed with AA and/or ICP. If italicised and underlined, the Na and Li data was obtained from 1993 historical data.

TABLE 13
Fly Ash Elemental Analyses

Station	Lethabo	Kendal	Duvha	Arnot	Majuba
Date	24-Apr-98	29-Apr-98	May-96	29-Jun-98	3&4-Oct-98
Filter type	ESP	ESP	FF & ESP	FF & ESP	FF
SO ₃ – Measured/Predicted	Unknown	0.3	0.4	1.2	N/A
Acid attack on fabrics?	N/A	N/A	Yes	No	No
Combustible matter (LOI) %	0.1	0.4	3.5	2.4	0.7
Silicon (as SiO ₂) %	55.7	50.8	52.6	54.6	58.2
Aluminium (as Al ₂ O ₃) %	31.6	32.9	30.7	23.7	23.8
Iron (as Fe ₂ O ₃) %	3.6	4.9	5.6	4.8	5.3
Titanium (as TiO ₂) %	1.6	1.6	1.7	1.3	1.6
Phosphorus (as P ₂ O ₅) %	0.21	0.73	0.9	0.19	0.4
Calcium (as CaO) %	4.1	5.6	5.6	7.7	6.4
Magnesium (as MgO) %	1.2	1.8	1.3	3.0	1.7
Sodium (as Na ₂ O) %	0.32	<u>0.06</u>	<u>0.14</u>	<u>0.31</u>	0.4
Potassium (as K ₂ O) %	0.5	0.6	0.5	0.6	1.0
Sulphur (as SO ₃) %	0.4	0.5	0.5	0.8	0.5
Manganese (as MnO) %	0.03	0.04	0.04	0.06	0.04
Lithium (as Li ₂ O) %	0.09	<u>0.032</u>	<u>0.015</u>	<u>0.024</u>	

The calcium (as CaO) was lower for those ashes that required lower than predicted SO₃ and where acid attack on the filter fabric took place. However, there was insufficient data to quantify a cut-off point for predictive purposes to adequately predict the SO₃ injection rate for Eskom, or South African, power utility coal ashes.

4.3 Ash Mineralogical Analyses

TABLE 5
Mineralogical Composition of Fly Ashes

Station	Lethabo	Kendal	Duvha	Arnot	Majuba
Date	24-Apr-98	29-Apr-98	May-96	29-Jun-98	3&4-Oct-98
Filter	ESP	ESP	FF & ESP	FF & ESP	FF
SO ₃ – Measured/Predicted	Unknown	0.3	0.4	1.2	
Acid attack on fabrics	N/A	N/A	Yes	No	No
Non-crystalline phases	Major	Major	Major	Major	Major
Crystalline phases					
Mullite Al ₆ Si ₂ O ₁₃	Major	Major	Major	Major	Major
Alpha-Quartz SiO ₂	Major	Major	Major	Major	Major
Maghemite Fe ₂ O ₃	Minor	Minor	Minor	Minor	Minor
Lime CaO	Minor	Minor	Minor	Minor	Minor
Anhydrite CaSO₄	N.D.	N.D.	N.D.	Minor	Minor
Rutile TiO ₂	N.D.	N.D.	Minor *	N.D.	Minor

N.D. = not detected

* = possibility only

Calcium in amorphous glass would be among the reported non-crystalline. Of the minerals detected, Lime (CaO) is the only one that will react with SO₃. The presence of Anhydrite (CaSO₄) is an indication of whether SO₃ has reacted with available calcium.

No Anhydrite was detected in Lethabo, Kendal, and Duvha fly ashes, indicating that the calcium was in a non-reactive form. Note that for Kendal, SO₃ FGC at an injection rate of 10 ppmv was in operation when the ash was sampled, whereas there was no SO₃ FGC for Lethabo and Duvha fly ashes.

It is concluded that the absence of Anhydrite in the presence of reported Lime can be used as an indicator that the calcium in the ash is wholly or partially in an unreactive form, such as in an amorphous glass. This can further be used to predict whether a fly ash will require less SO₃ than predicted by the Wahlco model, or FGC industry experience. The results indicate that this also applies for Lethabo.

4.4 Ash Alkalinity

Table 6 compares the alkalinity and reaction to H₂SO₄ results, for Lethabo, Kendal and Arnot ashes, with the ratios of measured to predicted SO₃ rates relative to Arnot.

TABLE 6
Ash Alkalinity

Station	pH @ 25°C	Alkalinity as CaCO ₃	Reaction with H ₂ SO ₄
		(0.02N HNO ₃)	(0.02N H ₂ SO ₄)
		mg/l	ml acid for pH 7.0
Lethabo	12.20	1171	11.45
Kendal	12.28	1349	14.10
Arnot	12.49	2783	20.75
	SO₃ – Measured / Predicted	Relative to Arnot	Relative to Arnot
Lethabo	Unknown	0.42	0.55
Kendal	0.3	0.48	0.68
Arnot	1.2	1.00	1.00

The Kendal ash had an alkalinity (as CaCO₃) significantly below that for Arnot. The reactions with H₂SO₄ show that the Kendal ash had less available, or “reactive”, calcium than the Arnot ash. Both these results are consistent with the Kendal fly ash requiring significantly less SO₃ FGC injection rate than Arnot.

The Lethabo ash had an alkalinity and reaction with H₂SO₄ slightly lower than that for Kendal. From this it was concluded that Lethabo would require significantly less SO₃ than was predicted (see 4.5 below). There was not sufficient information available to quantify by how much, but the ratio of “required” to “predicted” SO₃ injection would be less if not equal to Kendal and/or Duvha. It was concluded that the required SO₃ injection rate for Lethabo would be in the order of 0.3 to 0.4 of the predicted rate.

4.4.1 Buffering Capacity – Over-injection

Trials and commissioning experience with SO₃ FGC have shown that beyond the optimum injection rate a certain amount of over-injection can be tolerated without serious deterioration in ESP performance. Generally, over-injection is a waste of sulphur (required to produce SO₃), but is seldom a problem with ESP performance. In the case of Duvha and Kendal a rapid reduction in ESP performance occurred with even a slight amount of over-injection.

A revised description of SO₃ FGC mechanism would be that the SO₃ combines with the moisture in the flue gas and forms H₂SO₄, which reacts with a small amount of Lime (CaO) found in the ash to form Anhydrite (CaSO₄). The H₂SO₄ not used up reacting with the CaO forms an electrically conductive layer on the ash particles. The reaction of SO₃ (i.e. H₂SO₄) with the calcium gives a buffering protection against over-injection.

If the calcium is in a form that cannot react with H_2SO_4 most of the SO_3 will be available to condition the ash surfaces and less SO_3 would be required. However, the negative factor is that the buffering capacity of the ash to absorb over-injection of SO_3 is severely reduced. Over-injection will reduce the resistivity of ash to below the optimum resistivity and reduce ESP performance.

4.5 SO_3 Injection Rate – Lethabo

The predicted SO_3 injection rate curve for Lethabo, produced by Wahlco, is shown in Figure 7 [9.14 to 9.16].

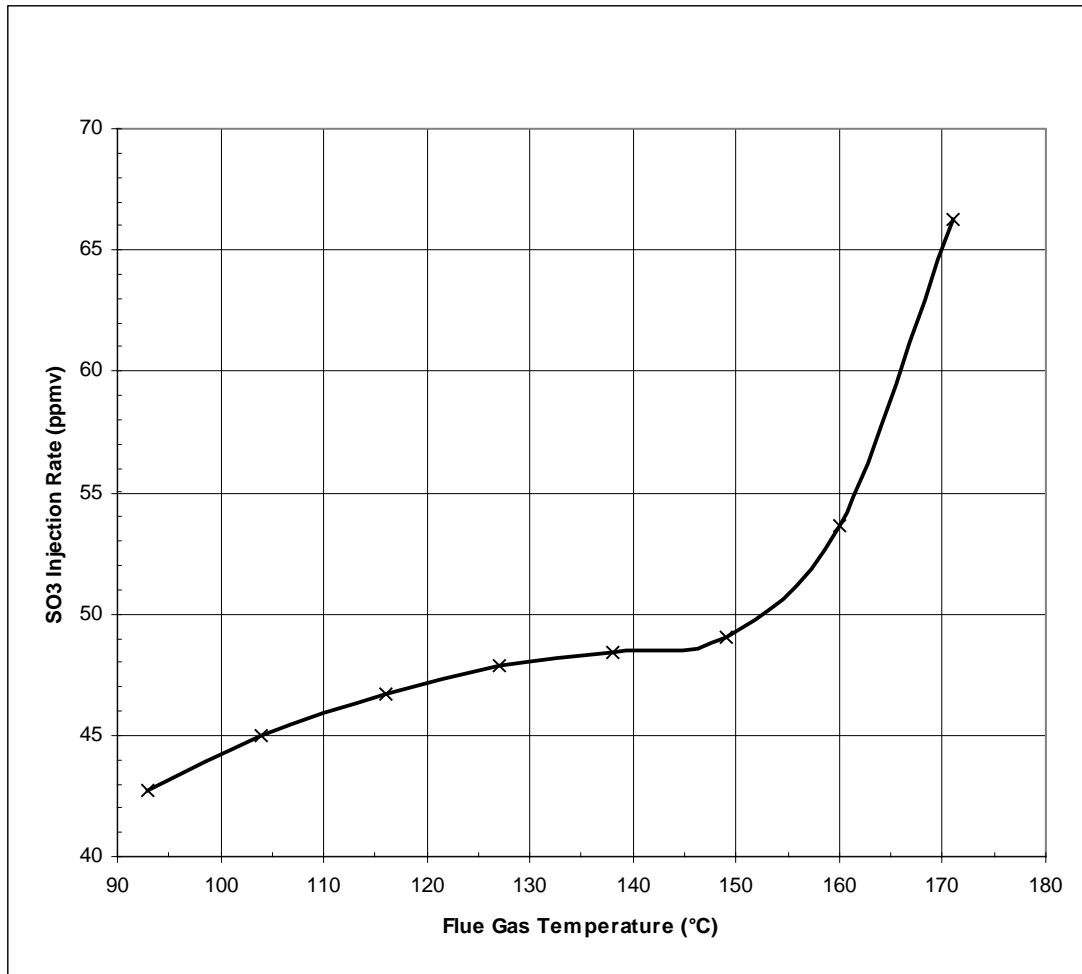


FIGURE 7
Predicted SO_3 Injection Rate vs. Temperature

At the time of the investigation, the back-end temperature at Lethabo could reach 150°C. The SO_3 injection rate curve predicts an injection rate of approximately 48 to 49 ppmv.

Since the ash alkalinity and reactivity with H_2SO_4 , for Lethabo fly ash, was just below that of Kendal, it was concluded that the proportion of “required” to “predicted” SO_3 would be similar to Duvha and Kendal, i.e. 0.3 to 0.4.

Based on the above, the SO_3 injection rate for Lethabo was predicted as 15 to 20 ppmv. The actual range of injection rates, for the permanent SO_3 FGC plant at Lethabo, is 18 to 22 ppmv. [6.21]

5. CONCLUSIONS

- 5.1 Elemental analysis of fly ash does not supply sufficient information to reliably predict the SO₃ FGC injection rate for ALL fly ashes.
- 5.2 Mineralogical analysis of fly ash, using X-ray diffraction spectroscopy, is a suitable and quick means of determining whether the calcium in a fly ash is not reactive to SO₃ in a flue gas and would thus require less SO₃ than predicted by models or industry experience. However, on its own, XRD does not supply sufficient information to reliably quantify the “required” to “predicted” proportion.
- 5.3 Alkalinity (as CaCO₃) and reactions with H₂SO₄ of fly ashes were shown to be a suitable method of determining whether the calcium in a fly ash is not reactive to SO₃ in a flue gas and would thus require less SO₃ than predicted by models or industry experience. In addition the method produces quantifiable results, which could probably provide sufficient information to reliably quantify the “required” to “predicted” proportion
- 5.4 The primary objective of the investigation was to determine the SO₃ FGC injection rate for Lethabo Power Station. More research and investigations will need to be conducted to develop a procedure and a model to reliably predict the SO₃ FGC injection rate for ALL fly ashes.

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