Optimization of Lime Dosage to Digestion at Alunorte Refinery Using Monte Carlo Methods

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Abstract

This paper presents work to establish ideal operational targets for lime to digestion at the Alunorte alumina refinery. To understand the impact of process variability on the required lime demand for both phosphate control and liquor stability, a Monte Carlo study was performed using a mass balanced model of the digestion process. Based on the results of these simulations, a fixed lime demand per tonne of dry bauxite was identified to satisfy greater than 95% of the conditions tested by the Monte Carlo simulation. Further to this, the impact of reduced lime to digestion flows on silica in liquor has been investigated, identifying no substantial risk. Based on this work, a new process controller has been proposed with the aim of reducing lime consumption by approximately 0.2 - 0.3 kg of CaO per tonne of bauxite.

Keywords: Lime; Monte Carlo; digestion; phosphate; control

1. Introduction

Lime is required on the red side of the process to ensure that phosphate does not cause undesirable scaling in the thickener overflow filters, and to guarantee liquor stability in the Clarification area in the form of soluble calcia [1]. In terms of the correct quantity to add, enough lime must be added to satisfy the stoichiometry of the phosphate to hydroxyl apatite reaction as well as the amount required to solubilize say, 20 ppm of CaO. It is important to realize that when more lime than the solubility requirement is added, more soluble calcia is not produced, rather more tricalcium aluminate hexahydrate (TCA6) is created according to:

$$3Ca(OH)_{2(s)} + 2Na[Al(OH)_4]_{(aq)} = 3CaO.Al_2O_3.6H_2O_{(s)} + 2NaOH_{(aq)} \qquad (1)$$

The exact mechanism for this reaction is not well understood and may involve a calcium carbonate or hydrocalumite intermediate species; but it is assumed based on solubility considerations that the final product is TCA6 as shown [2] [3].

This reaction (in this setting):

- Wastes lime
- Adds to the residue load
- Wastes alumina

The concentration of calcia achieved is merely a reflection of the solubility of TCA6. It is not known whether 20 ppm is the exact solubility concentration for Alunorte green liquor, but it is not far from spent liquor literature estimates [4]. Thus, 20 ppm might not necessarily be attainable, but based on the plant’s own historical data and the open literature, it seems a reasonable target to pursue.

Controlling the concentration is not so trivial when adding lime to the bauxite slurry feeding digestion, as the amount of liquor and bauxite slurry required will change, as will the amount of evaporation in the flash train between digester to blow off tank. A control strategy could look at all the relevant inputs and using some assumptions, calculate what the lime flow must be, but the time lag of the process in conjunction with the combination of so many measurement errors make this undertaking problematic.

An alternative approach is to understand just how significant the variation in these controlling parameters are to the required lime dosage. A useful tool for this study is a Monte Carlo simulation [5] whereby the natural variability of the relevant inputs can be simulated and the required lime flow solved. In this way, it can be discovered whether a fixed ratio of lime to the bauxite tonnage can be used to satisfy not just the phosphate demand (which makes sense to be based on the bauxite tonnage, as the phosphate exists in the bauxite), but also the liquor stability. This has been the aim of the present study.

2. Simulation Details

2.1. Model Set-Up

To investigate the impact of the different variables on lime consumption for phosphate and liquor stability, a mass balanced Microsoft ® Excel model was constructed which replicates essentially what process modelling software, (e.g. SysCAD [6]) does, but with a focus only on the digestion area of the process. A schematic of the process model is shown in Figure 1.

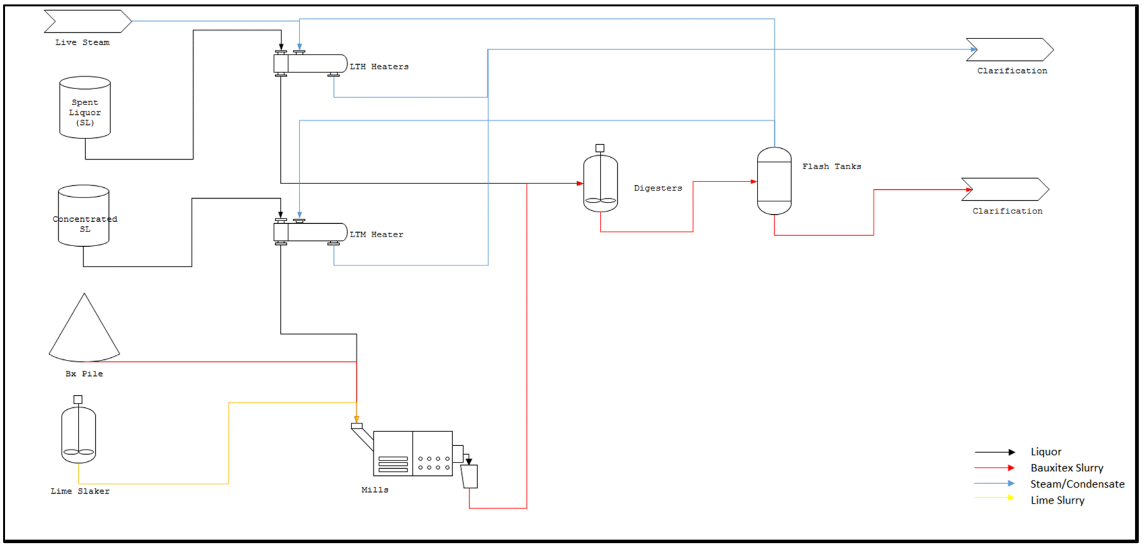


Figure 1. Block Flow Diagram of model under consideration. Note that condensate flows were not modelled but are shown for clarity.

Note that a flaw of this approach versus SysCAD is that the liquor loop is not closed (i.e. just a once through model). In the context of lime consumption investigations, this was not considered too great a sacrifice as the impact on overall liquor properties is not so great.

The process model functions in a very similar way to process modelling software, whereby the user inputs certain fixed variables, and then uses a solver algorithm to determine the values for the free variables. Rather than using a process modelling software's custom solving algorithms, this example depends solely on Excel's Solver ® to tune the freed variables until the output variable achieved the target value. For the simulation set in question, the principal fixed and free variable combinations are:

- BOR; tuned by bauxite slurry flow
- CaO concentration in blow off; tuned by lime slurry flow

Further, regarding the required energy balance, the SysCAD enthalpy correlations were used [7] and Microsoft ® Solver was again used to simultaneously calculate mixed stream temperatures to satisfy the energy balance. Note that the accuracy of the energy balance is less critical than the mass balance, in terms of the impact on soluble calcia and required lime dosage. Further, as the digester temperature is fixed based on plant data, and this is the main contributor to soluble calcia concentration leaving digestion, the key calculation is the evaporation extent (from digester to blow off tank) which again is dictated by the enthalpy correlations used.

The list of fixed variables and assumptions is shown in Table 1 (largely taken from SysCAD [6]). The main three of potential concern are the reaction conversions. They have been set at relatively arbitrarily high values and in reality, would change (slightly) based on the different inputs being fed to the model. Presently, for the sake of simplicity and assuming they would not have a large impact on the desired result, they have been fixed. It is suspected that the impact on lime demand would not be great as the total flows and evaporations would not be changing significantly with these conversions.

The variables allowed to vary based on a normal distribution, using historically determined averages and standard deviations are shown in Table 2.

Table 1. Fixed values for simulations.

Variable	Value	Unit
c_p Bx	0.8368	kJ/(kg.K)
Gibb Dissolution Enthalpy	385	kJ/kg
SG of Water	1	kg/L
Bauxite SG	2.8	kg/L
CaO SG	4	kg/L
$Ca(OH)_2$ SG	3.8	kg/L
c_p H_2O	4.18	kJ/(kg.K)
c_p Lime Solids	0.8368	kJ/(kg.K)
Specific Enthalpy of steam at 100 °C	2675.43	kJ/kg
c_p of steam at and above 100 °C	2.03	kJ/(kg.K)
Reactive Silica Extraction	97%	
DSP Conversion	97%	
Gibbsite Extraction	99%	

Table 2. Variables allowed to vary in the Monte Carlo Simulations.

Variable	Average	Std. Dev
% Solids in Bauxite (Bx) slurry	61.75	4.39
% Available Alumina	49.42	0.68
% Reactive Silica	4.26	0.32
% Moisture in Bx	12.44	1.87
%P_2O_5 in Bx	0.03	0.00
%Available Calcia in Lime	90	3
Spent Liquor (TTk) TC (gpL)	303.8	6.3
TTk A/TC	0.397	0.014
TTK TC/TA	0.980	0.005
TTk SiO_2/TC (gpL)	0.007	0.001
TTk Na_2SO_4/TC (gpL)	0.003	0.001
TTK NaCl/TC (gpL)	0.027	0.005
TTk TOC/TC (gpL)	0.007	0.002
TTk Ox/TC (gpL)	0.003	0.001
TTk Flow to LTH (m^3/hr @ 25 °C)	1068	66
TTk Temperature (°C)	75.9	7.9
Liquor to Mills (LTM) Temperature (°C)	105.4	7.5
Blow Off Ratio (BOR) (A/TC)	0.765	0.020
LTH Temperature after heating	172.33	4.65
Bauxite Temperature (°C)	25	3
Lime Slurry gpL Solids	230	36
Lime Slurry Temperature (°C)	70.31	8.58
Blow Off Temperature (°C)	107.15	1.28
% Liquor Evaporation (digestion to Blow off tank)	5.3%	0.5%
Target CaO Conc. (gpL)	0.02	0.005
LTM TC (gpL)	330	15

The only reactions under consideration are as follows:

Gibbsite Dissolution –

$$Al_2O_3.3H_2O_{(s)} + NaOH_{(aq)} = Na[Al(OH)_4]_{(aq)} \qquad (2)$$

Kaolinite Dissolution –

$$Al_2O_3.2SiO_2.2H_2O_{(s)} + 6NaOH_{(aq)} = 2Na_2SiO_{3(aq)} + 2Na[Al(OH)_4]_{(aq)} + H_2O_{(l)} \qquad (3)$$

DSP Precipitation –

$$6Na_2SiO_{3(aq)} + 6Na[Al(OH)_4]_{(aq)} + Na_2CO_{3(aq)} = \\ 3Na_2O.3Al_2O_3.6SiO_2.Na_2CO_3.6H_2O_{(s)} + 12NaOH_{(aq)} \qquad (4)$$

Slaked Lime to Apatite –

$$4Ca(OH)_{2(s)} + P_2O_{5(aq)} = Ca_3(PO_4)_2.Ca(OH)_{2(s)} + 3H_2O_{(l)} \qquad (5)$$

Note that only carbonate DSP (natrodavyne) is forming and no other cancrinite or alternative DSPs are being formed, which is in line with standard low temperature digestion logic. In reality, a distribution of sodalite/natrodavyne/noselite DSPs would form, but it is supposed that carbonate would be the dominant form based on related work in the literature [8] and as there is no quantitative way (openly available) to determine the distribution, it has been assumed completely carbonate DSP. The lime to apatite reaction is most likely an oversimplification, but as a consistent stoichiometry could not be identified in the literature (see for example the review by P. Smith [1]), this simple reaction scheme was elected.

2.2. Randomness and Normality

To perform Monte Carlo simulations, random numbers must be provided to the normal probability distribution (with historical average and standard deviation for the variable in question) so the value to be tested can be generated. To this end, an algorithm was identified and implemented via Visual Basic for Applications (VBA) into Excel, that provides more random number generation than Excel's default algorithms [9]. From the source consulted, the randomness is generated using the Mersene Twister algorithm, which was considered a good source by those authors. This attention to randomness and normality of the feed data may be a weakness in the study and could be an area of further investigation. For the results presented here, one thousand simulations were run using a custom-built VBA macro. The sensitivity to number of simulations has not been investigated.

2.3. Silica in Liquor Impact

Regarding the suggestion that silica incorporated TCAs (or hydrogarnets) can form, this has not been considered in the Monte Carlo simulations. However, as a separate exercise, using the results from the Monte Carlo simulation for lime demand, the reaction has been considered. The reaction is thought to proceed according to [10] (shown with slaked lime as reactant, but reference uses TCA6 as starting material):

$$\begin{gathered}3Ca(OH)_{2(s)} + nNa_2SiO_{3(aq)} + 2Na[Al(OH)_4]_{(aq)} = \\ 3CaO.Al_2O_3.nSiO_2.(6\text{-}2n)H_2O_{(s)} + (2+2n)NaOH_{(aq)} + nH_2O_{(l)}\end{gathered} \qquad (6)$$

Where n can take on a range of values (0-3), that are largely only relevant at high digestion temperatures around 250 °C. For 95 °C predesilication considerations, the value is typically thought of as 0.1 [1], while at low temperature digestion of 150 °C B. I. Whittington and C. M. Cardile [11] suggest that the value is likely < 0.5. Note that B. I. Whittington [12] also suggests in a separate paper that 0.6 represents a maximum for 250 °C digest, which perhaps renders the idea of 0.5 a bit difficult to accept. See in Figure 2 [11], that if one extrapolates to pertinent liquor conditions for Alunorte (TC approximately 300 gpL and carbonate concentration less than 10 gpL) it would seem that the value should be near n=0 (this is for 90-95 °C conditions though, not ~150°C).

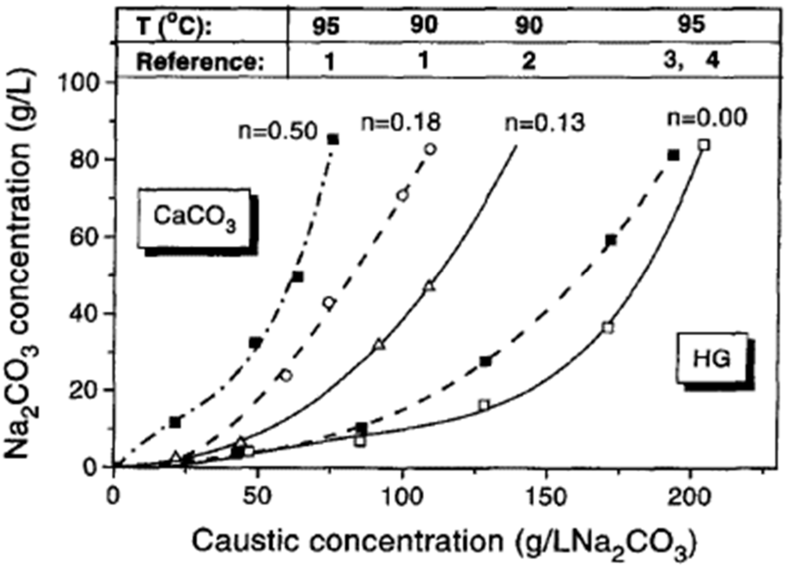


Figure 2. Stability regions for silica incorporated TCA6, or hydrogarnet (HG) versus calcite at different liquor conditions. The figure and associated references can be found in [11]

Suffice to say that the literature is not so clear on what the substitution should be at Alunorte's liquor conditions, and B. I. Whittington also has noted that heating rates can change the result somewhat as well [13]. For this study, n=0.5 and n=0.8 have been used to demonstrate the slight impact on silica removal in conjunction with the large lime and alumina losses associated with unrealistic silica substitution into TCA. Further to this, the amount of lime required to reduce the blow off silica by 0.1 gpL was investigated to understand what sort of lime and alumina penalty would be incurred to assist silica levels in an operational crisis.

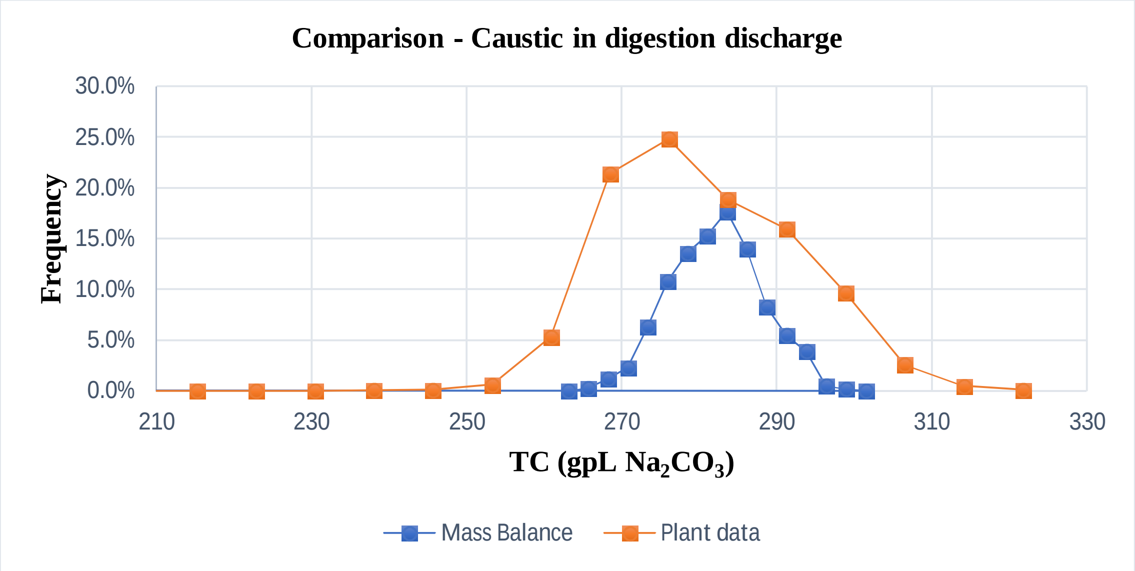
3. Results and Discussion

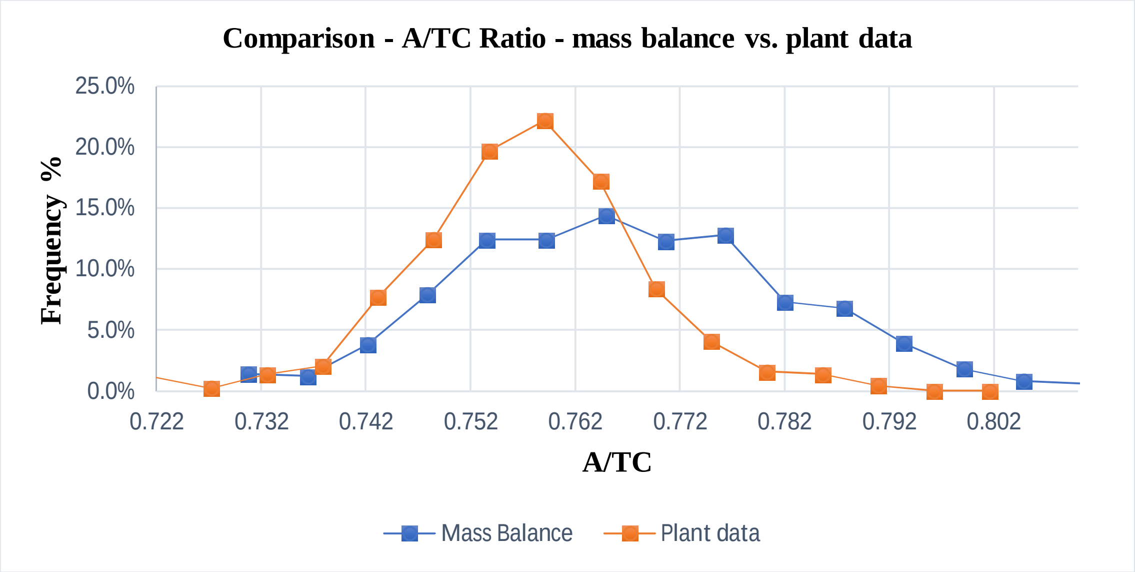
3.1. Simulation Results

Output plots from the simulations versus that of the actual plant data are shown in Figure 3. It can be seen that the modelled data corresponds reasonably well to that measured, with some data veering from the exact type of distribution due to not quite normal distribution. This is not thought to be a significant issue, as it is more encouraging that the modelled data is within the measured spectrum of values. Note that the blow off volumetric flow does not agree with that measured, but nor should it as the model has not included the effect of washer overflow (WOF) dilution. It can be seen that the difference is not so great which concurs with the relatively small flow of WOF versus that coming from the digesters. Note that the A/TC was not an output of the model but an input. The data is provided to highlight that the plant data was not as normally distributed, presumably due to thermodynamic limit on A/TC and the operational nature to push close to the practical maximum. The thermodynamic limit has not been imposed on the model and at times, the ratio has exceeded what is possible for the temperature. While nonsensical from an extraction standpoint, again, this is not considered detrimental to the lime flow study.

The principle variable of concern is that of slurry flow as that modelled clearly displays a shift from that measured. This may be due to the measured flow measuring at temperature versus the modelled reporting flow at 25 °C, but this issue has not been investigated further.

Given that the output data generally agrees with the modelled data, this gave the authors confidence that they could trust the associated lime demands predicted by the simulations. The distribution of CaO demand is shown in Figure 4. Looking at the aggregated data, it can be seen that a 0.8 kg/tonne of dry bauxite demand should easily satisfy > 95% of the scenarios indicated, with relatively little slope change for subsequent lime addition. Based on this result, 0.8 kg/t is prescribed as the target to utilize.





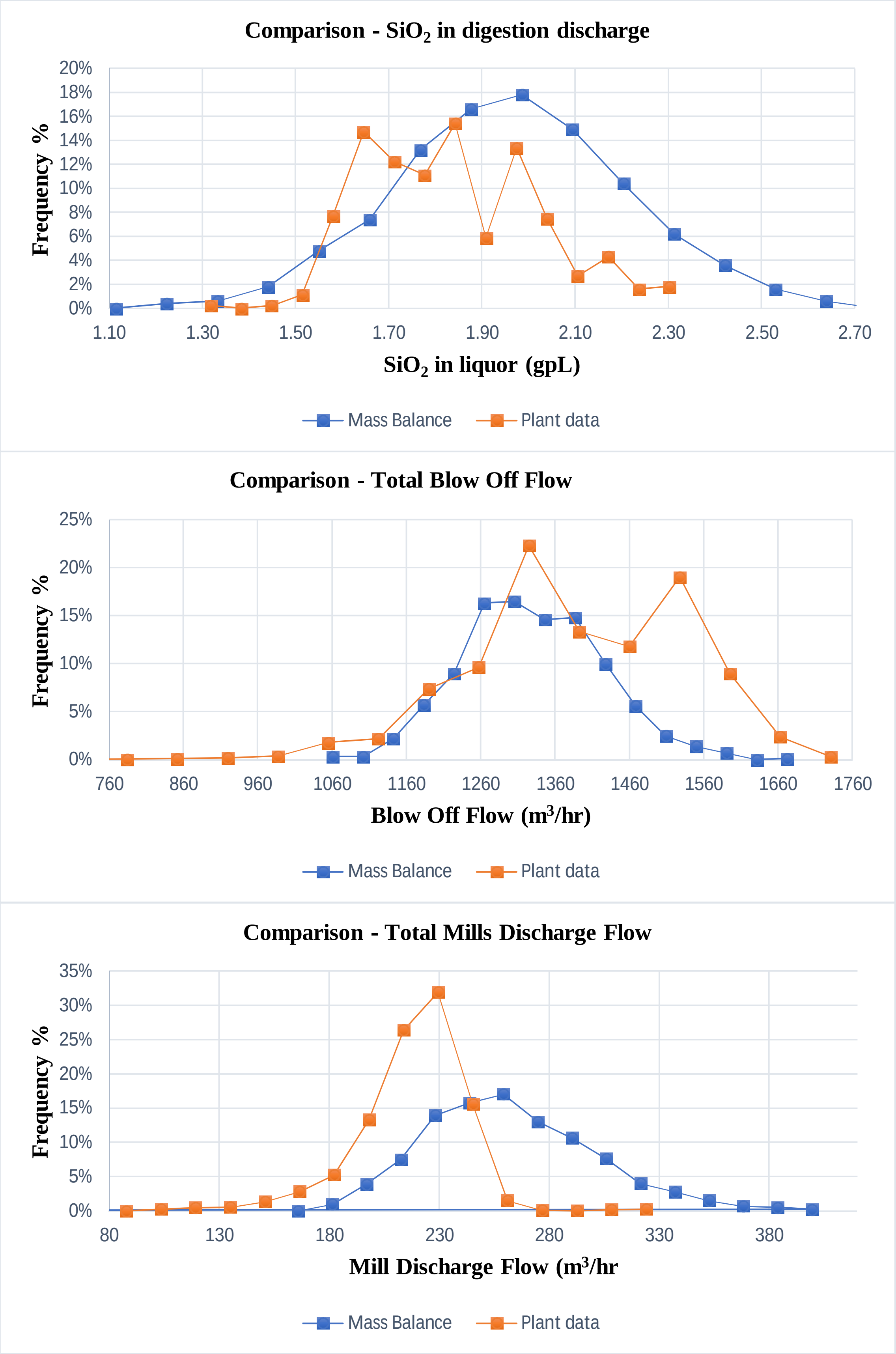


Figure 3. Some of the outputs determined by Monte Carlo simulation of mass balance model versus plant data.

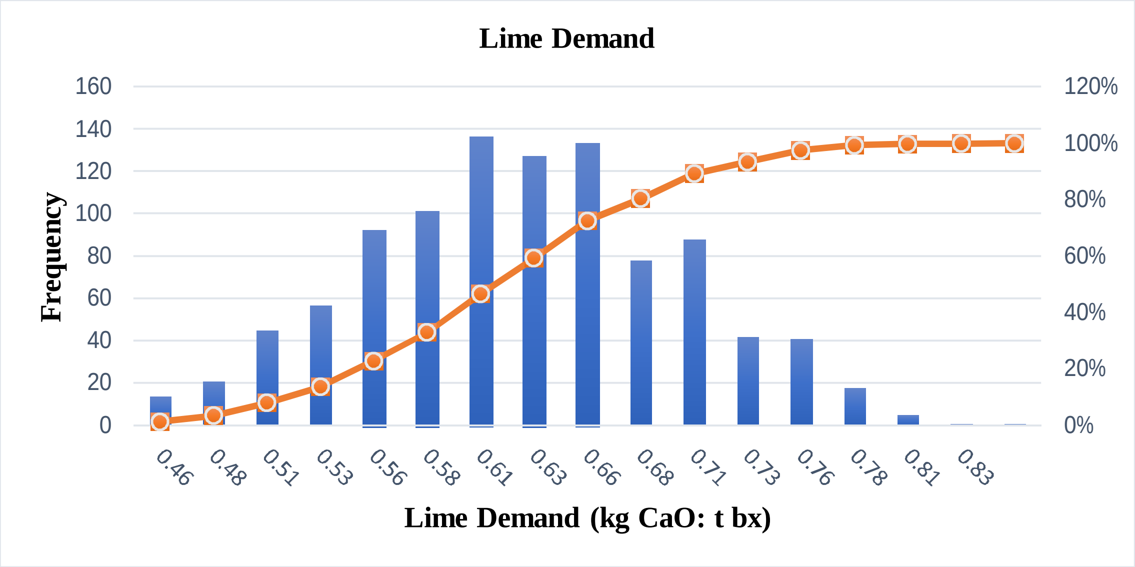


Figure 4. Model determined distribution of CaO demand per tonne of dry bauxite.

3.2. Opportunity

To investigate the opportunity of adjusting the lime to digestion target, the current usage was investigated. Alunorte has 7 digester lines, but broadly speaking they can be clustered into three groups (lines 1, 2 and 3; lines 4 and 5; lines 6 and 7). The consumptions for 2016 are shown in Figure 5 with the proposed target identifying the opportunity size. Further to this, the average and standard deviation of the historical data is shown in Table 3. Based on this data, it is apparent that an opportunity for lime reduction exists, combined with a serious need for control to reduce the variation in flow. The savings averages to approximately 0.2-0.3 kg CaO per tonne of bauxite and approximately 0.03% recovery improvement. Based on the opportunity identified, a simple control scheme has been proposed where the bauxite moisture, bauxite tonnage and slaked lime gpL (from lab, online and lab measurements respectively) are taken as inputs to generate the set point for the slaked lime flow.

Table 3. Average and standard deviation lime usage by line cluster.

Metric	Line 1/2/3	Line 4/5	Line 6/7
Average (kg/t)	1.18	0.81	1.07
Std. Dev (kg/t)	1.60	0.41	0.95

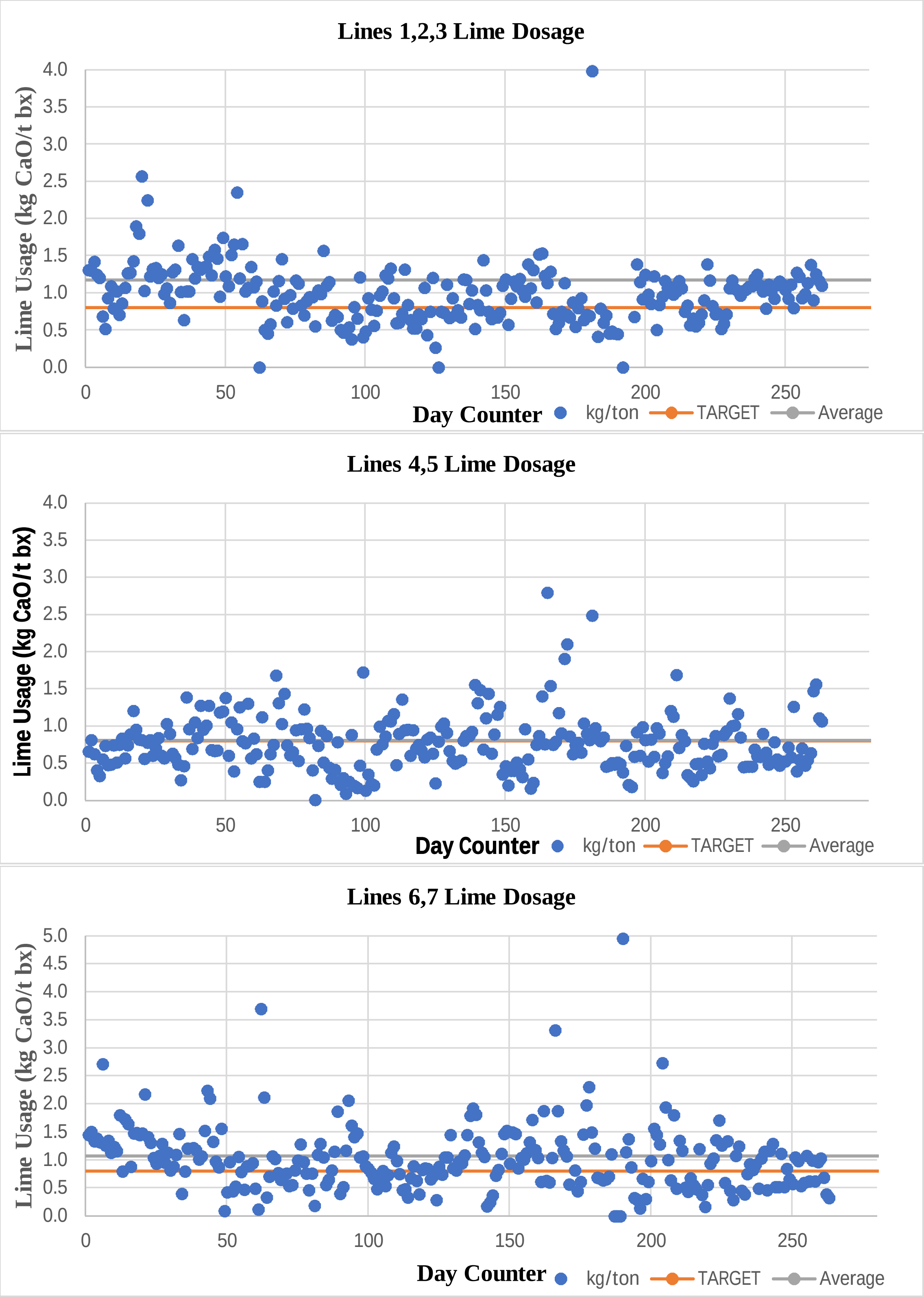


Figure 5. Lime demands in kg of CaO per tonne of dry bauxite. The x axis represents time, but is shown only as integers representing days (as opposed to exact dates).

3.3. Silica impact

Using the current lime usage and the suggested target, extraction penalties as well as silica in blow off were simulated. Further to these simulations, the required lime dosage to reduce the blow off concentration by 0.1 gpL was calculated. The results are shown in Table 4. It can be seen that for n=0.5 and n=0.8, changing from the current condition to the reduced target of 0.8 kg/t has a negligible impact on silica in blow off. Also note that to reduce the silica concentration from 1.6 to 1.5 gpL, the lime demand is considerably higher and would materially affect the alumina extraction as well as lime usage. Nonetheless, if in a silica crisis, this sort of study can be done to determine what dosage of lime is required (and what the other penalties will be). This data essentially confirms that silica considerations are of no consequence regarding the proposed change to lime dosage.

Table 4. Summary data for different simulations with differing silica substitutions at different lime dosages.

n = 0.8 in $3CaO.Al_2O_3.nSiO_2(6\text{-}2n)H_2O$			
	Current Condition	**Target Condition**	**Drop SiO_2 in BO to 1.5 gpL**
Total Al_2O_3 Ext	96.93%	96.96%	96.74%
Total SiO_2 Removed Liq	2.0%	1.1%	7.27%
SiO_2 Conc. (gpL)	1.59	1.60	1.50
CaO:Dry	1.043	0.80	2.556
Res/Bx	0.3102	0.3097	0.3132
n = 0.5 in $3CaO.Al_2O_3.nSiO_2(6\text{-}2n)H_2O$			
	Current Condition	**Target Condition**	**Drop SiO_2 in BO to 1.5 gpL**
Total Al_2O_3 Ext	96.93%	96.96%	96.60%
Total SiO_2 Removed Liq	1.2%	0.7%	7.08%
SiO_2 Conc. (gpL)	1.60	1.61	1.50
CaO:Dry	1.043	0.80	3.748
Res/Bx	0.3102	0.3097	0.3154

4. Conclusions

The lime demand for phosphate and liquor stability has been investigated by way of Monte Carlo simulation arriving at a lime requirement of 0.8 kg/t which represents a significant savings opportunity. Using the target identified from this study, a simple lime flow controller is being developed to guarantee the associated lime and alumina savings achievable. Further to this, the study has shown that a reduction in lime flow will have a negligible impact on liquor silica concentration leaving digestion, and demonstrated how to determine the necessary dose when in a crisis while simultaneously understanding the associated lime and alumina penalties.

5. References

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