The Effect of Dissolved Silica in Bayer Liquor Titration

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Abstract

To understand the differences in dissolution kinetics between alumina and silica minerals in Bayer liquor, it is essential to measure both soluble alumina and silica with accuracy. Based on irreconcilable mass balances established by liquor measurement, the impact of dissolved silica on Bayer liquor titration analytes was investigated. This paper reports the quantitative impact of dissolved silica spanning 2.0 to 4.6 gpL SiO_2 on spent, intermediate and green liquor analytes, namely – free caustic, sodium aluminate and sodium carbonate. It also suggests a hypothesis to explain the impacts via silica interference with alumina and sodium carbonate titration reactions.

Keywords: Silica; analytical bias; Bayer liquor; titration.

1. Introduction

Liquor in a typical Bayer process alumina refinery is composed largely of water, sodium hydroxide, sodium aluminate and sodium carbonate. While there are a number of different ways to analyze for these 'essential' Bayer liquor components, (titration [1] [2]), thermometric techniques [3], discontinuous flow analysis [4]), the vast majority of alumina producers utilize some version of potentiometric titration, either based on the Watts-Utley method [1] or the more recently developed Connop-Gran method [2].

The analysis of Bayer liquor via standard titration techniques is not without its inaccuracies, but this is typically accepted due to the greater need for precision [2] [5] in aiding refinery process control. However, in more fundamental laboratory studies which necessitate mass balances or understanding of process kinetics, it is not acceptable to have high precision alone. The focus shifts to accuracy to ensure that mass balance can be achieved. During such laboratory investigations centering around bauxite digestion, it was found that a mass balance between liquor and solid could not be achieved, so the effect of soluble silica was investigated. Silica was seen as a key contributor to the mass balance issues owing to:

1) The body of work identified in the literature which had already pointed to silica as a source of inaccuracy
2) the considerable range of silica concentrations encountered in a laboratory bauxite digestion.

Elaborating further on this second point, the silica concentration can vary considerably owing to the kaolin dissolution and DSP precipitation reactions which occur during a conventional bauxite digestion:

$$Al_2O_3.2SiO_2.2H_2O_{(s)} + 6NaOH_{(aq)} = 2Na[Al(OH)_4]_{(aq)} + 2Na_2SiO_{3(aq)} + H_2O_{(l)} \qquad (1)$$

$$\begin{gathered}6Na[Al(OH)_4]_{(aq)} + 6Na_2SiO_{3(aq)} + Na_2CO_{3(aq)} = \\ 3Na_2O.3Al_2O_3.6SiO_2.Na_2CO_3.6H_2O_{(s)} + 12NaOH_{(aq)}\end{gathered} \qquad (2)$$

The carbonate form of DSP has been shown here, which is most pertinent to the liquor conditions at Alunorte.

An added contributor to the perhaps more pronounced effects noted in these digests, is the mineralogy of the Paragominas bauxite processed at Alunorte refinery. The reactive silica level is rather high (~4.7%), so the soluble silica can perhaps be more pronounced than other bauxite sources.

While the literature has noted an impact of silica on the standard titration analytes (see Table 1 below), it was not clear whether the effect was the same in spent and green liquor. Further, it was also unclear why there were some inconsistencies in the reported 'biases' and whether they stemmed from differences in methods or analysis. Finally, the majority of historical work had seemed to focus exclusively on the impact on alumina analysis, not considering total caustic (TC), free caustic (FC), or carbonate (or total alkali (TA)) independently.

Table 1. Impact of soluble silica on Bayer liquor titration methods reported in literature.

Reference	**Titration Notes**	**[SiO_2]/ [Al_2O_3] Tested**	**Titrated Al_2O_3 [g]**	**Al_2O_3/TC**	**Analyte/s Investigated**	**Bias (gpL analyte per gpL SiO_2)**
L. J. Snyder [6]	Tartrate for bound caustic and KF for remaining $Al(OH)_3$	0.002-0.120	0.1489	1	Al_2O_3	0.5-8.6
A. H. Bushey [7]	KF then OH back titration	0.012-0.420	0.2	Unclear	Al_2O_3	-0.3-1.1
H. L. Watts and D. L. Utley [8]	$BaCl_2$ for carbonate, tartrate for bound caustic; KF with OH back titration	0.008-0.195	0.1284	0.313	Al_2O_3, FC, TC, Na_2CO_3	Al_2O_3: -0.2-0.37 TC: -0.5-0.1 FC: -0.15-0.31 Na_2CO_3: 0.03-0.9
H. L. Watts [9]	KF	0.007-7	0.004-0.11	1	Al_2O_3	-0.18-6.25
L. Tomscanyi and G. Lanyi [10]	*ibid*	0-0.263	0.038	N/A	Al_2O_3	~0.15

Based on these curiosities, combined with the fact that a quantitative correction could not be found that was applicable to the conditions being tested at Alunorte, the aim of this work was therefore to quantify the impact of soluble silica on the standard titration analytes (alumina (A), total caustic (TC) and total alkali (TA)) and verify if the impact was in fact the same for spent and green liquors corresponding to pre and post bauxite digestion conditions.

2. Methodology

2.1. Experimental Methodology

Refinery spent or green liquor was obtained on the same day of analysis and manipulated volumetrically to achieve the target conditions via addition of a sodium silicate solution (46.3 ± 1.4 gpL). An intermediate liquor was produced by diluting the green liquor with raw caustic solution from the refinery (~1000 gpL TC) and water. The table of conditions investigated is shown below in Table 2. To ensure against DSP precipitation, the silicate solution was added dropwise which ensured that any precipitates forming had time to re-dissolve. The solution was confirmed stable only by visual inspection. Each condition was made up in triplicate (i.e. 3 volumetric flasks per condition investigated) so as to understand the precision of the analyses. The soluble silica was measured via the traditional Molybdate blue method [11]. This should perhaps be considered superior to ICP techniques as it avoids the measurement of any colloidal silica which can report to the ICP analysis. The standard liquor properties were analyzed by a Metrohm-automated-titration based essentially on the Watts-Utley [1] procedure.

Table 2. Summary of liquors prepared with synthetic silica solution.

Liquor	Vol Refinery Liquor	Vol of SiO_2 solution	Final Volume of Solution
Spent/Intermediate/ Green Liquor	45	1	50
	45	2	50
	45	3	50

2.2. Weighted Least Squares (WLS)

In regard to processing the data into quantitative correlations, the method chosen was weighted least squares where the weights were derived from the standard deviation of each triplicate measurement of the response variable. In this case, the response variable is the measured analyte concentration in the standard titration with the input variable the silica concentration.

This analysis assumes a linear relationship exists between the inputs (SiO_2 concentration, X, a 3x2 matrix) and the outputs (measured analyte concentration, Y, a 3x1 matrix):

$$\boldsymbol{Y} = \boldsymbol{X} \cdot \boldsymbol{\beta} + \boldsymbol{\varepsilon} \tag{3}$$

Where: $\boldsymbol{\beta}$ is the coefficient matrix (a 2x1 matrix)
$\boldsymbol{\varepsilon}$ is the error term accounting for noise in the data (a 3x1 matrix).

For ordinary least squares (OLS), the best estimate of the coefficient matrix is simply:

$$\widehat{\boldsymbol{\beta}}_{\boldsymbol{OLS}} = \left(\mathbf{X}^{\mathbf{T}} \cdot \mathbf{X}\right)^{-\mathbf{1}} \cdot \mathbf{X}^{\mathbf{T}} \cdot \mathbf{Y} \tag{4}$$

Which produces estimates of the output variable according to:

$$\widehat{\boldsymbol{Y}} = \widehat{\boldsymbol{\beta}} \cdot \boldsymbol{X} \tag{5}$$

A crucial assumption of OLS is that the variance of the error term, ε is:

$$\boldsymbol{Var(\varepsilon)} = \boldsymbol{\sigma^2 \cdot I} \tag{6}$$

Where σ^2 is a measure of the variance of each observation against that predicted:

$$\boldsymbol{\sigma^2 = \sum_{i=1}^{n}(\hat{y}_i - y_i)^2} \tag{7}$$

In the case of weighted least squares (WLS), the variance of the error term is better described using a weighting, ω_i, the measured variance of y_i:

$$\boldsymbol{Var(\varepsilon) = \sigma^2 \cdot \omega} \tag{8}$$

$$\boldsymbol{\omega = \begin{bmatrix} \omega_1 & 0 & \cdots & 0 \\ 0 & \omega_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \omega_n \end{bmatrix}} \tag{9}$$

Where, in the case of a triplicate measurement of y_i, the measured variance is of course:

$$\boldsymbol{\omega_i = \frac{1}{2}\sum_{j=1}^{3}\left(y_{i,j} - \bar{y}_i\right)^2} \tag{10}$$

Where the subscripting in y signifies the j-th measurement of the i-th data point.

Based on these considerations of unequal variances of each data point (i.e. heteroskedasticity), it can be shown [12] that the best estimate of the coefficient matrix is in fact:

$$\boldsymbol{\hat{\beta}_{WLS} = \left(X^T \cdot \omega \cdot X\right)^{-1} \cdot X^T \cdot \omega \cdot Y} \tag{11}$$

The variance of the fitted coefficients is accordingly:

$$\boldsymbol{Var\left(\hat{\beta}_{WLS}\right)_i = \sigma^2 \cdot \left[\left(X^T \cdot \omega \cdot X\right)^{-1}\right]_{ii}} \tag{12}$$

WLS fits were applied to the data sets investigated for spent liquor (SL), intermediate liquor (Int Liq) and green liquor (GL). Further to this, the same approach was utilized when comparing the biases determined for each liquor type to develop a correlation which uses the best bias based on the measured concentrations of the titration analytes.

3. Results

The average and standard error of triplicate analysis of the base liquors are shown in Table 3.

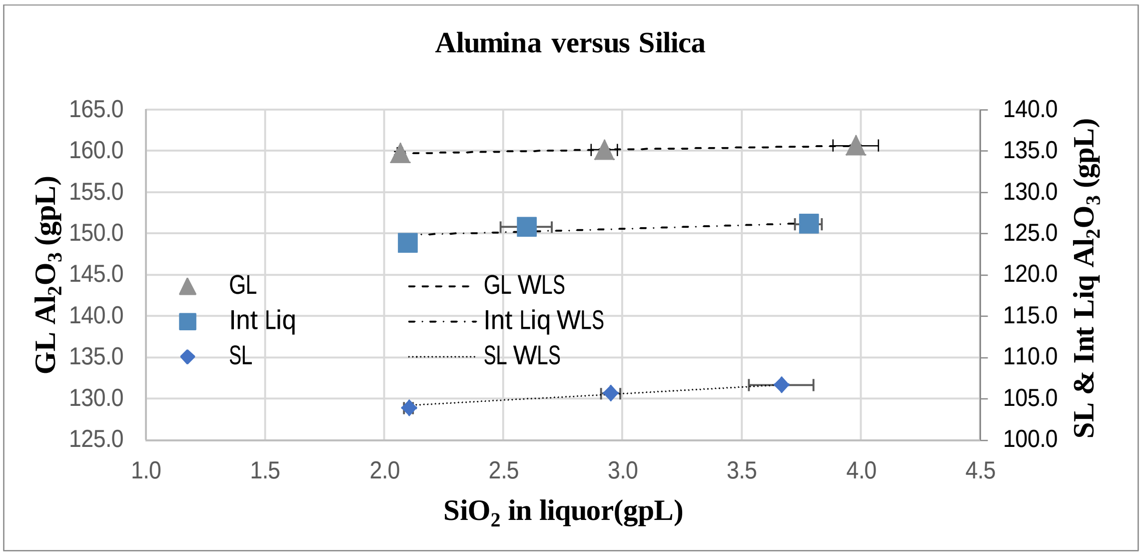
Table 3. Start liquor conditions used for silica dosing.

Liquor Condition	**A/TC**	**Al_2O_3**	**TC**	**Na_2CO_3**	**SiO_2**
SL	0.372 ± 0.001	114.4 ± 0.1	307.6 ± 1.0	8.1 ± 0.4	1.49 ± 0.05
Int Liq	0.487 ± 0.000	137.6 ± 0.1	282.3 ± 0.1	7.3 ± 0.6	1.30 ± 0.02
GL	0.718 ± 0.001	175.7 ± 0.7	244.7 ± 0.5	2.1 ± 0.4	1.21 ± 0.03

Figure 1 shows directly the impact of soluble silica on the key analytes. A positive trend is observed for alumina and sodium carbonate in all liquors, but it can be seen that the size of the bias seems to diminish as the liquor gets greener. See Table 4 for specific quantities. The free caustic and TC data is somewhat more erroneous, and the trend in fact shifts from positive to negative as the liquor becomes greener. Despite the unusual comparison between alumina and TC slopes, the A/TC bias remains positive, but diminishes somewhat as the liquor gets greener owing to the TC negative bias overpowering the positive impact of alumina. While the intermediate liquor errors do overlap somewhat with spent and green, it can be seen in Figure 2 that there is a clear difference (comparing three standard errors) between the determined biases for all the analytes in spent versus green liquor.

Table 4. Silica Bias and intercepts of analyte versus silica plots with one standard error.

Analyte	**SL**		**Int Liq**		**GL**	
	Bias	Intercept	Bias	Intercept	Bias	Intercept
A	1.56 ± 0.04	100.99 ± 0.13	0.81 ± 0.19	123.17 ± 0.61	0.47 ± 0.00	158.78 ± 0.00
FC	0.37 ± 0.09	167.54 ± 0.25	-0.32 ± 0.16	124.70 ± 0.4	-0.60 ± 0.11	57.00 ± 0.36
Na_2CO_3	3.05 ± 0.24	1.99 ± 0.63	2.24 ± 0.68	3.24 ± 1.52	0.96 ± 0.13	5.47 ± 0.39
TC	2.33 ± 0.18	271.43 ± 0.53	1.21 ± 0.47	250.23 ± 1.14	-0.15 ± 0.10	222.13 ± 0.31
A/TC	3.36 ± 0.00 x10^{-3}	0.369 ± 0.003	3.24 ± 0.00 x10^{-3}	0.483 ± 0.002	2.51 ± 0.00 x10^{-3}	0.715 ± 0.002



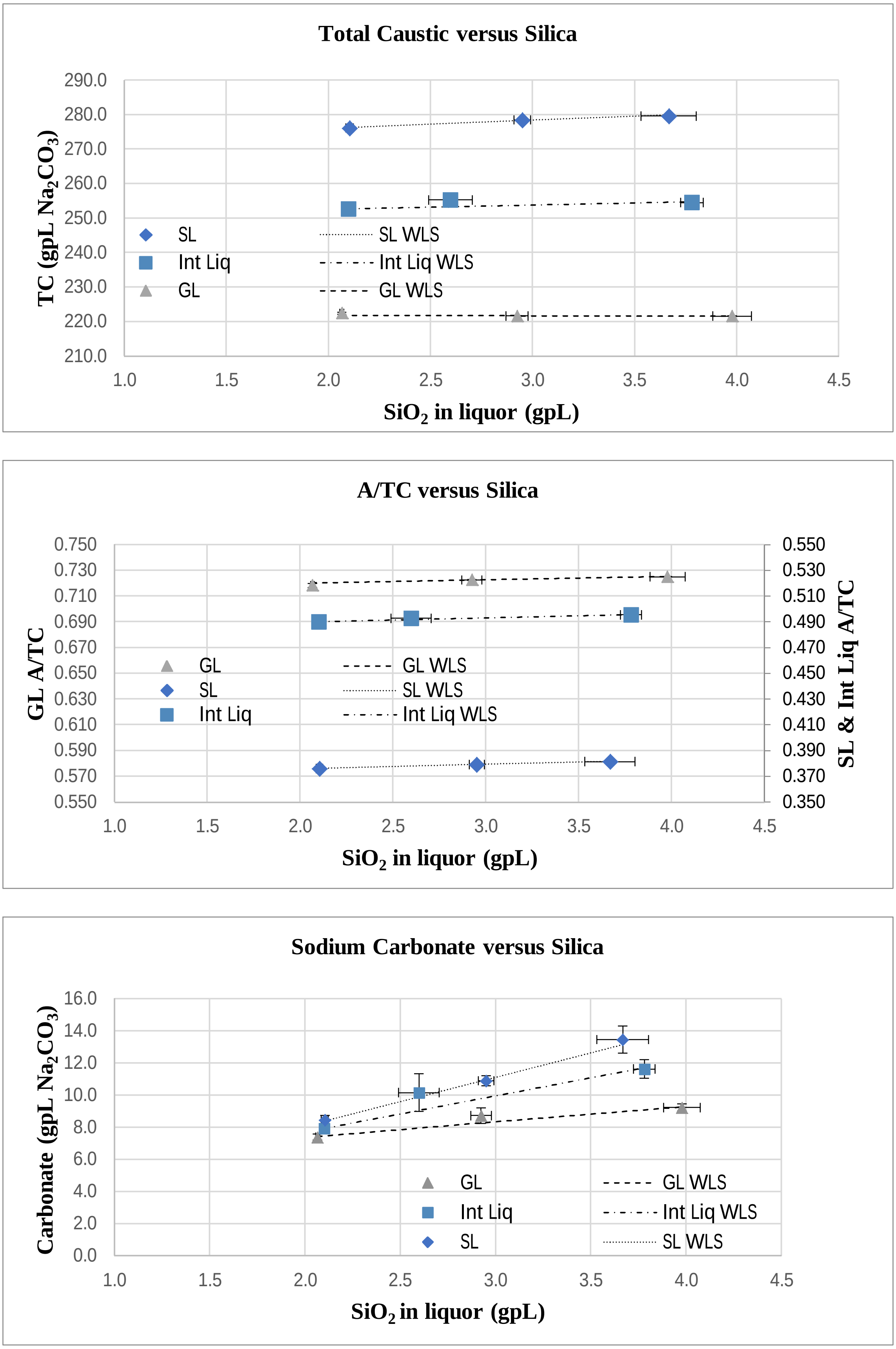


Figure 1. Key titration analytes versus soluble silica with weighted least squares fits.

In an attempt to quantify the way that the silica bias changes depending on the liquor type, the slopes of the lines in Figure 1 were plotted against their intercepts. This approach inherently assumes that the intercept of these plots corresponds to the ‘true’ value of the analyte as there is no bias inflicted from soluble silica. It was found that the analytes showed trends when plotted in this regard, as shown for alumina in Figure 3 and detailed for all the analytes in Table 5.

This approach was not extended to carbonate owing to the intersection of all plots at a very-near common value of 7 gpL. The aforementioned approach would mean that a measure of 7 gpL carbonate could correspond to a variety of different ‘real’ values, which is of course nonsensical. Thus, for sodium carbonate only, as the silica impact does not offer a great deal of impact to mass balance consideration, an average impact of all three slopes reported has been adopted for correction.

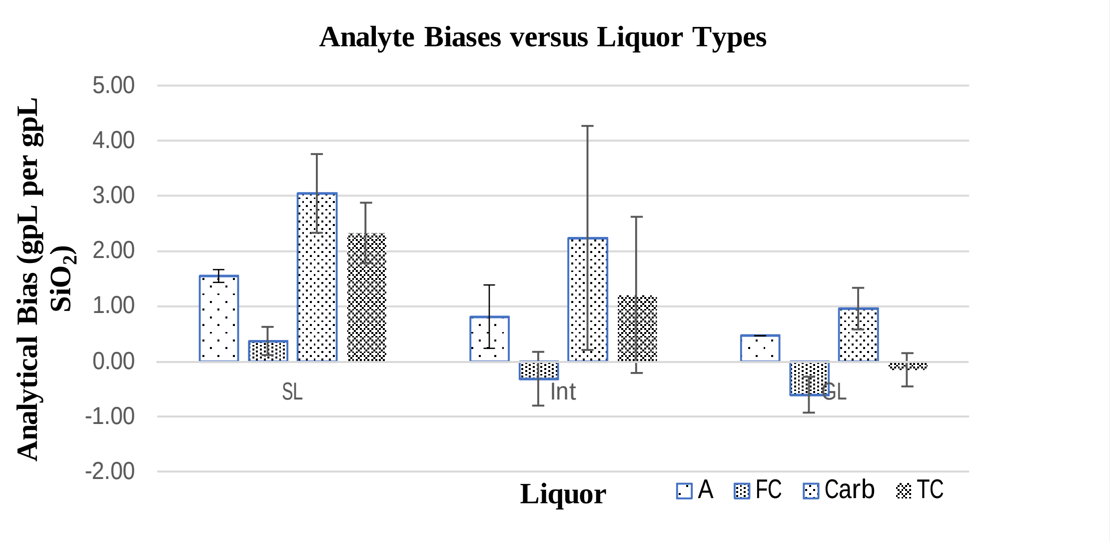


Figure 2. WLS Bias found for each analyte in the different liquors used, with three standard errors as error bars. (SL = Spent liquor, Int = Intermediate liquor, GL = Green liquor).

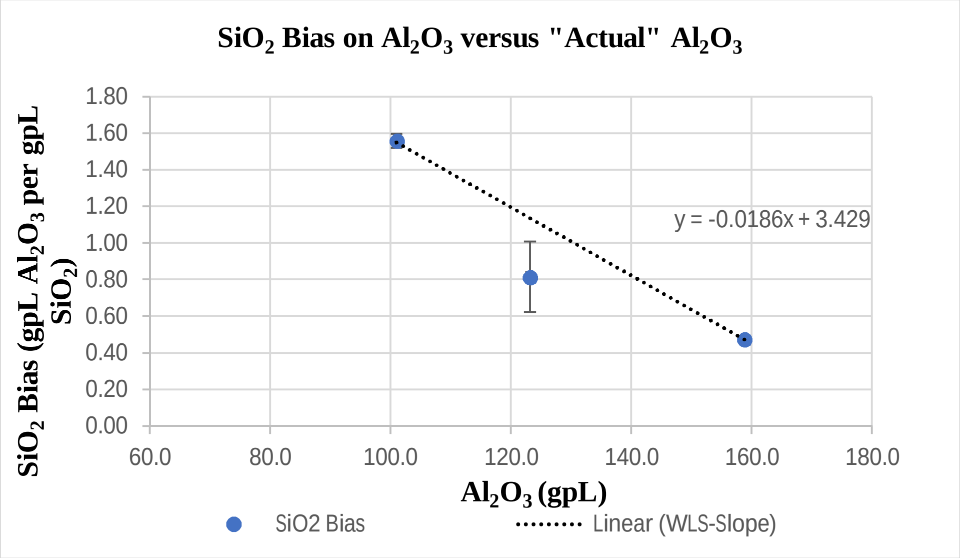


Figure 3. The impact of ‘Actual’ alumina concentration on the silica bias observed.

The fitted line in Figure 3 is from WLS analysis. A stronger impact is noted for a spent liquor (lower Al_2O_3) than a green liquor.

Table 5. Slopes of bias versus intercept plots with percentage error, by WLS treatment.

Analyte	Slope	%Error on Slope
A	$-1.86\text{x}10^{-2}$	1.16
FC	$8.80\text{x}10^{-3}$	3.90
TC	$5.03\text{x}10^{-2}$	0.46
A/TC	$-2.11\text{x}10^{-3}$	0.00

4. Discussion

Before attempting to rationalize how silica is impacting the titration analytes reported, it is useful to review the specifics of the titration practice at Alunorte. While based on the fundamentals of Watts-Utley [1] using potentiometry with Metrohm automated equipment, the procedure is not an exact replica, so it is worth restating here. For a standard spent or green liquor, liquor is diluted with sodium tartrate to liberate one bound caustic from the aluminate ion according to [2] [8]:

$$[Al(OH)_4]^-_{(aq)} + nT_{(aq)} = [Al(OH)_3\text{-}T_n]_{(aq)} + OH^-_{(aq)} \qquad (13)$$

Where T represents the tartrate radical.

This material is then titrated to two end points (using HCl), the first corresponding to the TC or free caustic plus the bound caustic liberated from the aluminate ion; followed by a second endpoint corresponding to the carbonate to bicarbonate reaction:

$$CO_3^{2-}{}_{(aq)} + H^+_{(aq)} = HCO_3^-{}_{(aq)} \qquad (14)$$

Both of these endpoints are detected by online inflection methods. Subsequent to these endpoints, KF is added to liberate the three other hydroxyls from the aluminate complex by forming a cryolite precipitate [1] [2]:

$$[Al(OH)_3\text{-}T_n]_{(aq)} + 6KF_{(aq)} = K_3AlF_{6(s)} + 3KOH_{(aq)} + nT_{(aq)} \qquad (15)$$

This liberated hydroxide is then titrated to the carbonate end point to allow for the aluminate to be determined, also by an inflection detection method. It is acknowledged that the use of tartrate is not ideal for carbonate determinations, versus gluconate [1], but the concentration of carbonate is very low in Alunorte liquor and because of this, both the precision and accuracy are deemed less critical. Further, via the introduction of dynamic endpoint detection [5], the concerns originally raised [1] [8] regarding the accuracy of the carbonate endpoint detection in the presence of the alumino-tartrate complex are less concering.

When investigating the impact of silica on the titration method practiced, it seems essential to consider first that there most likely is an interference in the KF reaction based on the quantity of information reported in the literature. F. Vieböck and C. Brecher [13] proposed the following interference,

$$SiO_{2(aq)} + 2H_2O_{(l)} + 6KF_{(aq)} = K_2SiF_{6(aq)} + 4KOH_{(aq)} \qquad (16)$$

Which is further supported by the comment from Bushey [7] that “silicate forms fluosilicate and is converted to silica during the back-titration”. This idea of silica reacting with KF to liberate hydroxide and form a fluosilicate is corroborated by Lawson et al [14] (and references therein, particularly G. Hafter [15]) who utilized this phenomenon to measure soluble silicate in alkaline solutions for the soap industry.

Further to these comments, L. Tomscanyi and G. Lanyi [10] suggested essentially the same interference, when working on titration techniques to measure available alumina in bauxites and residues, while unusually suggesting the soluble silica exists as silicic acid in solution. More recent work, for example that of T. W. Swaddle [16], (and references therein), would suggest that silica exists in solution as some form of deprotonated silicic acid as suggested by the pKa values of pKa(1) = 9.5-9.9, pKa(2) ~12.7 and pKa(3) ~15. This would imply that in a typical Bayer solution with pH 15, silica would exist as triple deprotonated silicic acid, (Na_3SiO_4H) which perhaps protonates to varying extents as the pH reduces during the standard liquor titration. Given the overlap of the pKa(1) with that of the sodium carbonate to bicarbonate reaction (10.3) [17], this seems a plausible explanation for the positive bias noted for the carbonate reaction.

In the same work, T. W. Swaddle [16] suggested the possibility of aluminosilicates forming in solution according to:

$$HO_{(4-x)}SiO_x{}^{x-}{}_{(aq)} + Al(OH)_4{}^{-}{}_{(aq)} = (HO)_3AlOSiO_x(OH)_{3-x}{}^{(x+1)-}{}_{(aq)} + H_2O_{(l)} \qquad (17)$$

Evidence for these species has only been reported in rather dilute solutions and in Si/Al ratios that are not as likely in the Bayer industry (~5 gpL TC, 0.1 gpL Al_2O_3, 0.06-0.3 gpL SiO_2). Unfortunately, while some sort of species presumably must form like this as part of the desilication product precipitation, there does not seem to be a lot of evidence pertinent to the liquors in question to this analysis and so its existence has not been considered here.

Silica can also be impacting the reported TC via interference in the tartrate reaction which liberates free hydroxide. As there are two alumina reactions that occur during the titration (namely, tartrate addition to liberate bound caustic and KF addition to liberate the remaining three hydroxides), it is possible that the alumina is being impacted to different extents. This could account for the observed differences in TC and FC. T. R. Rinder and E. H. Oelkers [18] have shown that the analysis of silica by the molybdate blue method can be impacted by tartrate addition, due to either an interference between tartrate and the molybdate complex or tartrate with soluble silica. If the latter is true, then it is possible that during the Watts-Utley titration for standard Bayer properties, silica is also reacting with tartrate when it is added to liberate bound caustic according to:

$$SiO_3OH^{3-}{}_{(aq)} + mT_{(aq)} = [SiO_3\text{-}T_m]^{2-}{}_{(aq)} + OH^{-}{}_{(aq)} \qquad (18)$$

In attempting to form a hypothesis that explains the observed phenomena (i.e. positive bias on alumina and carbonate in all liquors, positive impact on FC and TC in spent liquor, but negative in green liquor), an explanation involving alumina and sodium carbonate bias alone would be simplest. If the degree of silica interference to the tartrate reaction for liberating ‘bound caustic’ is different to that of the interference with KF, the TC (and FC) would be impacted by the algorithm, as opposed to a direct impact on the free caustic titration. As this idea seems the simplest explanation, the current hypothesis follows:

1) The carbonate is biased up by virtue of silicate anion protonation in the appropriate pH range of 9.5-10.5, probably according to:

$$NaOSi(OH)_{3(aq)} + HCl_{(aq)} = Si(OH)_{4(aq)} + NaCl_{(aq)} \qquad (19)$$

2) The alumina-tartrate formation reaction that liberates bound hydroxide is impacted by soluble silica, presumably by silica consuming tartrate according to reaction 18.
3) The KF addition reaction also reacts with SiO_2 and increases the A content, in a way similar to reaction 16.
4) The relative impact of tartrate silica bias to KF bias shifts in spent to green liquor, for reasons unknown.

That last aspect of the hypothesis is perhaps the most perplexing and presumably cannot be resolved without, ideally, some extra substantiating evidence. It may be tempting to suggest that as the alumina concentration increases, the ability of silica to scavenge the tartrate and KF reduces, but both reagents are in significant excess for all liquor conditions. Perhaps the kinetics of one or both processes are negatively impacted by the higher alumina concentration, but again; such subsequent hypotheses cannot be furthered without some form of extra evidence.

It must be remembered that all of the silica bias impacts shown here are both native to the titration process practiced as well as the concentration ranges tested. The purpose of the study centered around reconciling mass balance issues for digestion data, and the biases shown here have been applied to this data. Extension of these correlations to understand yield impacts are the obvious next step, but this concentration range is outside of that reported here. Therefore, based on the size of the impact noted here, extension of the work to more pertinent concentration ranges for other plant conditions is the natural next step.

5. Conclusions

Soluble silica has an impact on the determination of the reported composition of a liquor, which in many ways simply corroborates what has been noted in historical work. A group of correlations for this effect have been developed that quantify the impact for liquor of varying alumina concentrations. A hypothesis regarding how the alumina and carbonate reactions are affected has been put forward which seems to reconcile all the observations noted in the data reported. These hypotheses are preliminary and require subsequent testing to confirm or deny their veracity. Further to identifying the need to understand the phenomena occurring, next steps have been proposed to better understand the soluble silica impact in all liquor concentrations pertinent to the refinery, not just that of bauxite digestion, to quantify impact on key metrics, such as yield.

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