

## 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<sub>2</sub> 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.

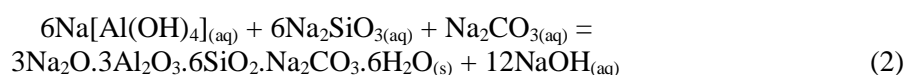
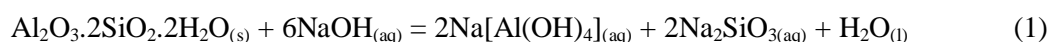
### 1. Introduction

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:



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 <sub>2</sub> ]/[Al <sub>2</sub> O <sub>3</sub> ] Tested	Titrated Al <sub>2</sub> O <sub>3</sub> [g]	Al <sub>2</sub> O <sub>3</sub> /TC	Analyte/s Investigated	Bias (gpL analyte per gpL SiO <sub>2</sub> )
L. J. Snyder [6]	Tartrate for bound caustic and KF for remaining Al(OH) <sub>3</sub>	0.002-0.120	0.1489	1	Al <sub>2</sub> O <sub>3</sub>	0.5-8.6
A. H. Bushey [7]	KF then OH back titration	0.012-0.420	0.2	Unclear	Al <sub>2</sub> O <sub>3</sub>	-0.3-1.1
H. L. Watts and D. L. Utley [8]	BaCl <sub>2</sub> for carbonate, tartrate for bound caustic; KF with OH back titration	0.008-0.195	0.1284	0.313	Al <sub>2</sub> O <sub>3</sub> , FC, TC, Na <sub>2</sub> CO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> : -0.2-0.37 TC: -0.5-0.1 FC: -0.15-0.31 Na <sub>2</sub> CO <sub>3</sub> : 0.03-0.9
H. L. Watts [9]	KF	0.007-7	0.004-0.11	1	Al <sub>2</sub> O <sub>3</sub>	-0.18-6.25
L. Tomscanyi and G. Lanyi [10]	<i>ibid</i>	0-0.263	0.038	N/A	Al <sub>2</sub> O <sub>3</sub>	~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) 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<sub>2</sub> 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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