AA10 - Kinetics of Silica Dissolution from Post Differential Extraction Slurry

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Abstract

Differential Extraction is a process that aims to reduce the caustic consumption of refineries when using high-silica bauxite. The process maximizes the extraction of alumina in a fast digestion and reduces the dissolution of silica in the liquor. Subsequently, the residue slurry undergoes a rapid process of solid/liquid separation (S/L) to stop the silica reaction. The objective of this work was to evaluate the extent of silica dissolution post-S/L separation under plant wash conditions. Shrinking Core Model (SCM) heterogeneous kinetics model was chosen for the kinetics evaluation. For this, temperature (71–95 ºC), solids concentration (50 g/L to 150 g/L), and residence time (0–30 min) were study. Factorial design of experiment was applied to evaluate the statistical influence of the factors on the response variable. The results showed that the limiting step of the dissolution process was the surface chemical reaction, and statistical analysis indicated that temperature and residence time mostly affect the silica reaction of the solids post-S/L.

Keywords: Silica dissolution, Slurry, Digestion, Differential extraction.

1. Introduction

Kaolinite content in bauxite, namely reactive silica, represents the main factor related to the loss of caustic soda in the Bayer process. This silica mineral dissolves in the caustic solution and will re-precipitate as a variety of sodium aluminum silicates (known as dessilication products – DSP) which are then discarded in the bauxite residue, implying significant cost increases, or even becoming uneconomical to process high silica content bauxites [1,2]. To reduce this loss, several technological strategies have been studied and implemented [2]. Differential Extraction is one of these technologies. The process takes advantage of the different kinetics of alumina and silica reactions, aiming to maximize the alumina extraction in a fast digestion step reducing the silica dissolution. After the digestion process, the slurry undergoes a rapid solid-liquid separation process to completely interrupt the silica reaction. The separated solids are washed to recover soluble soda before dewatering in press filters to be disposed. The process is claimed to reduce caustic soda consumption by approximately 50 % compared to a conventional Bayer process. [3,4].

Once the solids are separated from the green liquor and mixed with wash water is expected that negligible silica dissolution occurs. In this context, this work aims to evaluate the extent of dissolution of silica after solid-liquid separation considering the refinery conditions to ensure no dissolved silica impact on the product and scaling in downstream equipment in the Bayer loop. The silica dissolution kinetics was evaluated using the overflow liquor from a refinery washer under the following conditions: temperature (71 – 95 ºC), solids concentration (50 g/L to 150 g/L), and residence time (0–30 min). A statistical study was also carried out using a Design

of Experiment (DOE) Factorial to evaluate the influence of the control variables on the dissolution of silica.

2. Experimental

2.1 Materials

The experiments were carried out using a representative sample of bauxite from Mineração Paragominas. To perform the digestion a plant spent liquor was used. For the solids washing tests it was collected the overflow from the last washer of the plant clarification circuit. These materials were characterized and kept stored in conditions to avoid changing their characteristics.

2.2 Design Of Experiments

The dissolution test consisted of two main steps: the first was fast digestion (differential digestion and fast S/L separation), and the second step was the solids washing in which the dissolution tests of the silica were performed. Figure 1 presents a schematic of the test scope.

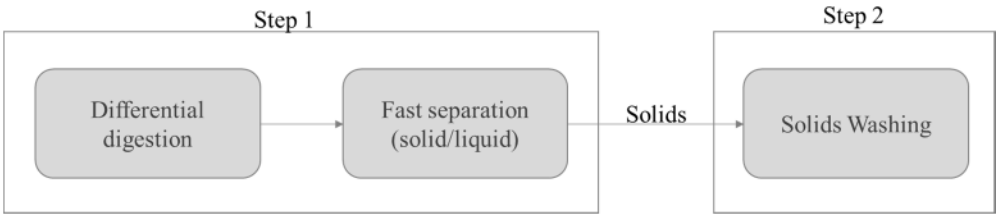

Figure 1. Test diagram.

A factorial design of the experiments (DOE) with analysis of variance (ANOVA) was considered with a significance level of $\alpha = 0.05$, post-dissolution SiO_2 concentration as the main response variable, and the following control variables and levels:

- solids concentration (g/L): 50; 100; 150
- retention time in washing (min): 4; 17; 30
- temperature (°C): 71; 83; 95

In total, 33 runs were performed, 24 referring to the 2^k factorial points with 3 replicates and 9 referring to the repetitions in central point.

2.3 Kinetics Analysis

The dissolution kinetics analysis considered that during the silica reaction on the solid-liquid interface no solid species were produced. Thus, the Shrinking Core Model (SCM) heterogeneous kinetics model was selected for the kinetics evaluation.

The SCM model consists of three main steps: The first step is the diffusion of liquid reactants towards the liquid-solid reaction surface by external diffusion; the second step is the reactions at the interface; the last step is the diffusion of products from the interface to the liquid by internal diffusion between intermediate layers. As the reaction takes place, the solid particle is consumed, reducing its size (Figure 2).

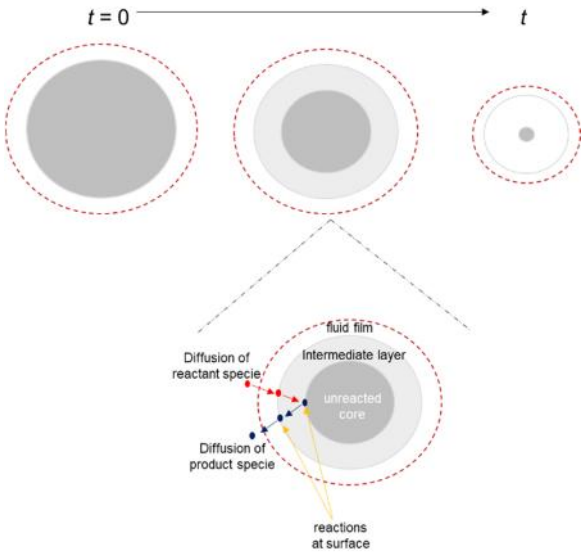

Figure 2. Heterogeneous kinetics – SCM [5].

The mathematical models considered are represented by equations (1) and (2): the chemical reaction is the limiting one (Equation (1)); diffusion through the intermediate layer is the limiting factor (Equation (2)).

$$1-(1-\alpha')^{1/3} = kt \quad (1)$$

$$1-2/3\alpha'-(1-\alpha')^{2/3} = kt \quad (2)$$

Where:

k apparent rate constant

t reaction time, min

α' reaction length calculated according to Equation (3).

$$\alpha' = SiO_2 \text{ concentration in solution / } SiO_2 \text{ concentration on original sample} \quad (3)$$

3. Results

3.1 Kinetics Analysis

The correlation coefficients (Table 1) showed that the surface reaction model fitted the experimental data better than the diffusion model through the intermediate layer.

Table 1. Correlation coefficients.

Condition*	R^2 (diffusion intermediate layer)	R^2 (surface reaction)
50s71T	0.8593	0.9707
50s95T	0.8055	0.9657
150s71T	0.9026	0.9927
150s95T	0.975	0.985
100s83T	0.8039	0.9608

*s = solids concentration; T = temperature

Note that the correlation coefficient values (R^2) are higher for the model where the chemical reaction is the limiting step. It is noteworthy that to all conditions of solids concentration and temperature mainly, the limiting model of surface reaction fitted better to the data.

Some observations are highlighted below:

- The experiments were carried out separately, keeping solid concentration and temperature constant for each run. In this way, the SCM model could be applied to describe the reaction kinetics.
- Dynamic processes tend to reduce the thickness of the boundary layer, thus reducing the influence on the overall reaction rate by external diffusion – diffusion through the fluid film [5, 6]. Based on that, the external diffusion effect in the kinetic analysis was disregarded.
- As the limiting step is the surface reaction, it indicates the temperature has a significant effect on the reaction rate. In this case, increasing the fluid velocity and modifying the particle size does not influence the dissolution reaction rate [5, 6, 7].

Figures 3 and 4 show the graphical behavior of the models fitted to the experimental data.

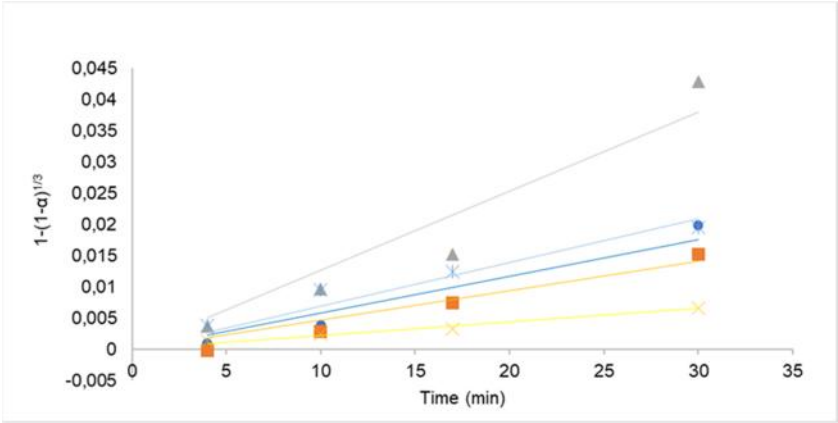

Figure 3. Linear relationships of $1-(1-\alpha')^{1/3}$ vs t (limiting step: surface reaction).

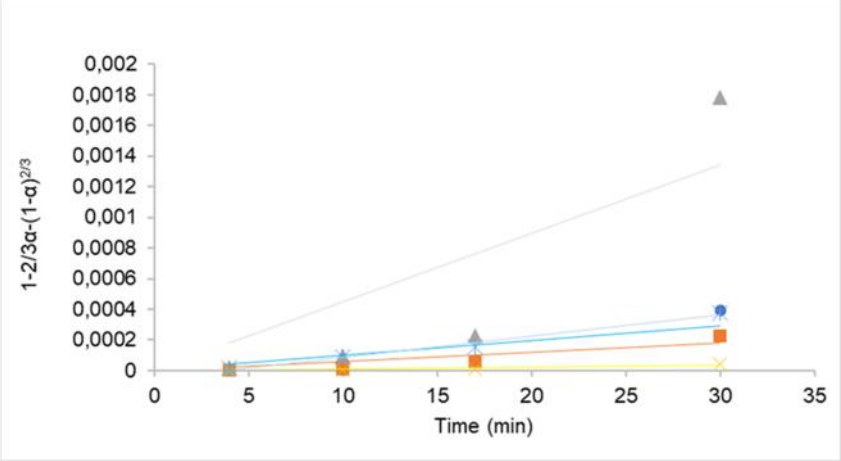

Figure 4. Linear relationships of $1-2/3\alpha'-(1-\alpha')^{2/3}$ vs t (limiting step: intermediate diffusion).

Figure 5 qualitatively shows the behavior of the apparent rate constant. Note that for the same solids concentrations and an increase in temperature from 71 ºC to 95 ºC, the apparent rate increases, indicating a higher rate of silica dissolution.

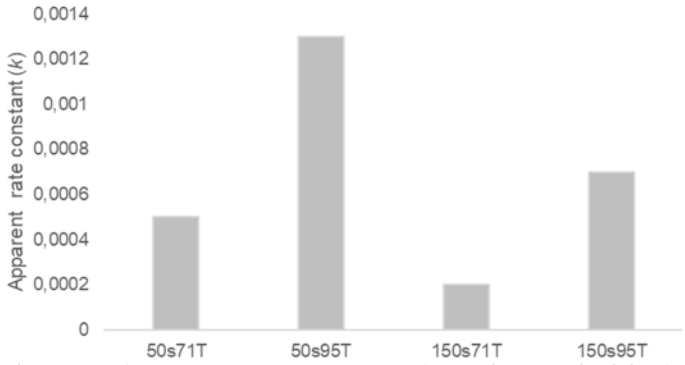

Figure 5. Apparent rate constant (reaction as limiting).

3.2 Influence of Control Variables on Silica Dissolution

The results of the statistical analysis regarding the effects are presented in Table 2.

Table 2. Effects of control variables on the % silica dissolution response.

	Effect	Coeff	p-value
Constant		1.942	0.000
Solids (g/L)	-1.389	-0.695	0.006
Temperature (ºC)	2.131	1.066	0.000
Time (min)	3.483	1.742	0.000
Solids (g/L).Time (min)	-1.533	-0.766	0.003
Temperature (ºC).Time (min)	1.557	0.778	0.003

It is noteworthy that the analysis of the factorial experiment considered the Stepwise method for regression, considering $\alpha = 0.05$ for the inclusion or exclusion of terms in the mathematical model. Based on the results obtained and analyzing the control variables separately, it is observed that:

- Solids concentration (g/L) has a negative effect on the response (silica dissolution) – when moving from a lower level to a higher level, there is a reduction in the dissolution percentage of approximately 1.4 %, that is, when the concentration of solids reduces dissolution.

- Temperature (ºC) has a positive effect on the response – when moving from a lower level to a higher level, the percentage of silica dissolution increases by approximately 2.1 %, that is, when increasing the temperature rises to dissolution.

- Retention time of washing (min) has a positive effect on the response – when moving from a lower level to a higher level, the percentage of silica dissolution increases by approximately 3.5 %, that is, when the time amounts to dissolution.

The ANOVA test (Table 3) was performed on the results of percentage of silica dissolution to assess the significance of the control variables. Note that only statistically significant variables and interactions are present in the ANOVA analysis (rejected null hypothesis). It is important to note that there is no lack of model fit (p-value > 0.05), so the model describes the experimental data well (Equation (4)).

Table 3. ANOVA.

	df	SS (Adj.)	MS (Adj.)	F-value	p-value
Solids (g/L)	1	11.581	11.581	8.76	0.006
Temp (ºC)	1	27.250	27.250	20.60	0.000
Time (min)	1	72.794	72.794	55.03	0.000
Solids (g/L)*Time (min)	1	14.097	14.097	10.66	0.003
Temperature (ºC)*Time (min)	1	14.541	14.541	10.99	0.003
Lack of fit	2	5.348	2.674	2.44	0.109

$$R.SiO_2\ Diss\ (\%) = 1{,}942 - 0{,}00615\ Solids\ (g/L) + 1{,}066\ Temp\ (ºC) + 1{,}742\ Time\ (min) - 0{,}766\ Solids\ (g/L) * Time\ (min) + 0{,}778\ Temp\ (ºC) * Time\ (min) \quad (4)$$

The Pareto diagram (Figure 6) confirms the greater significance of the control variables effects – concentration of solids, temperature, and time on the dissolution of silica (response). Considering the individual effects of the control variables, the greatest influence on silica dissolution in descending order occurs as follows: time > temperature > solids concentration. Interaction effects of solids concentration and temperature with time were also significant.

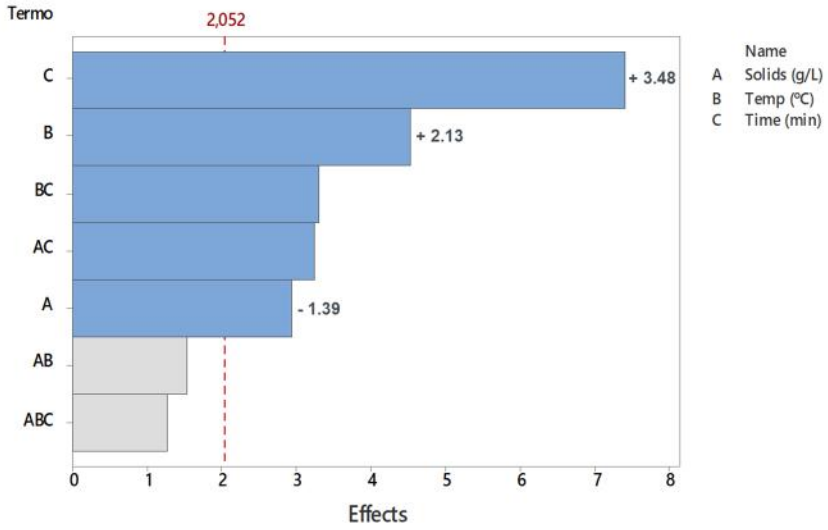

Figure 6. Pareto diagram.

The contour surfaces are shown in Figures 7, 8 and 9. Figure 7 presents the contour graph for the % silica dissolution as a function of temperature and solids concentration. The control variable Time was set at the lower level corresponding to 4 min, as in this condition the effect of time on silica dissolution is minimized (effects table). This condition is considered desirable, because depending on the rapid separation process, a slurry washing step is included. In this sense, the washing water would not interfere with the solubilization of the reactive silica. In this work, the overflow from last washer was used, which has a caustic content. Thus, the dissolution of silica in the residue after differential digestion is undesirable for the process and should be minimized. Note that lower dissolution values are obtained at lower temperatures and lower concentrations of solids.

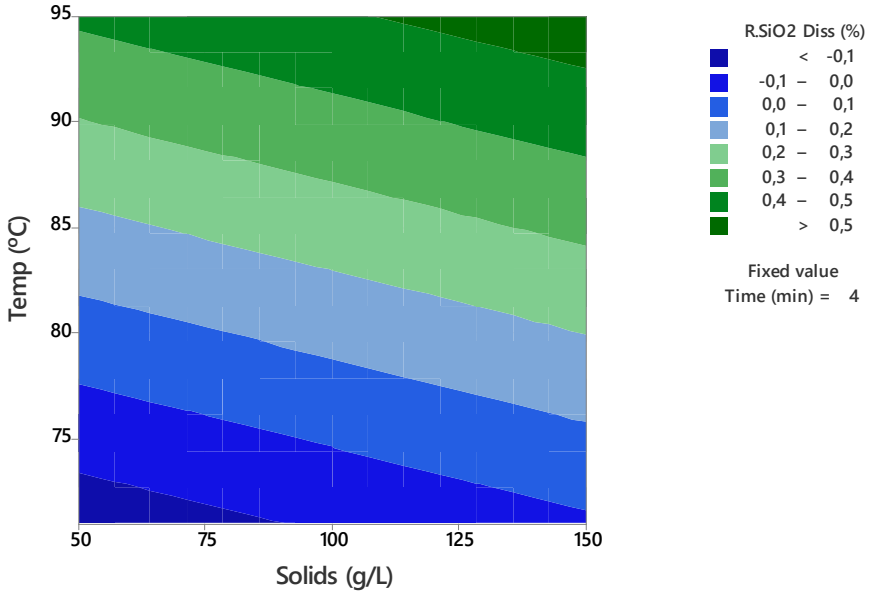

Figure 7. Contour plot % silica dissolution as a function of temperature and solids concentration; time control variable fixed at its lower level.

Figure 8 presents the contour plot for the percentage of silica dissolution as a function of time and solids concentration, with temperature set at the lower level (71 ºC), as in this condition the effect of temperature on silica dissolution is minimized (effects table). Note that lower dissolution values are obtained in less time and higher concentrations of solids. The dissolution reduction behavior is highlighted for higher solids concentrations. One can question what could have caused this behavior, since the greater the availability of solids it is inferred that the greater the dissolution could be, however, the following can be highlighted:

- As observed in the heterogeneous kinetic analysis, silica dissolution is influenced by the chemical reaction step, so the positive effect on dissolution occurs mainly by raising the temperature and reaction time.
- In figure 9, the positive effect of temperature on dissolution is more evident, reaching values greater than 4 %.

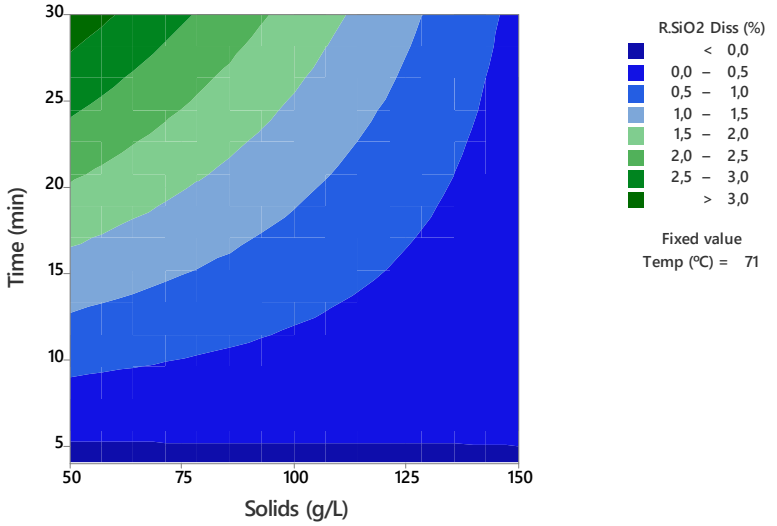

Figure 8. Contour plot % silica dissolution as a function of time and solids concentration; control variable Temperature fixed at its lower level.

Figure 9 presents the contour plot for the percentage of silica dissolution as a function of Time and Temperature with Solids concentration set at the upper level (150 g/L), as in this condition the effect of solids concentration on silica dissolution is minimized (effects table). Note that lower dissolution values are obtained in less time and lower temperatures.

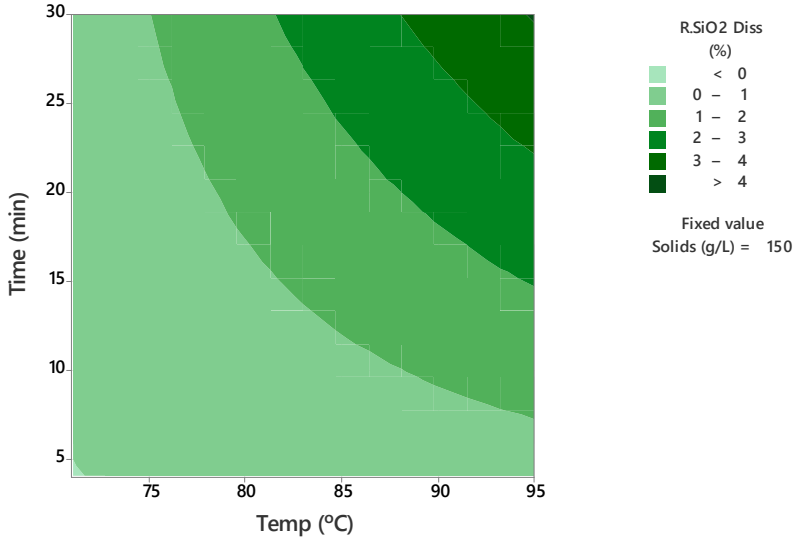

Figure 9. Contour graph % silica dissolution as a function of time and temperature; control variable solids concentration fixed at its upper level.

4. Conclusion

Heterogeneous kinetics was analyzed according to the SCM and demonstrated that the limiting step of the silica dissolution reaction in the post-S/L solids washing step is the surface reaction. Thus, the temperature has a significant effect on the reaction. The test showed that silica dissolution has positive effects when the process temperature and residence time during solids washing are higher. The solids concentration showed a negative influence on the dissolution therefore, the increase in the charge had a lower influence on the dissolution. Statistical analysis indicated positive effects of temperature and residence time, thus corroborating the kinetic analysis performed.

This work collaborates to the overall evaluation of the differential extraction technology, demonstrating that it is possible to restrict the silica dissolution during the fast digestion and from the solids after the solid-liquid separation. The tested confirmed a negligible dissolution extent for the conditions set for this application.

5. References

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