CHEMICAL REACTION ENGINEERING IN THE BAYER PROCESS

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Abstract

Chemical reaction engineering provides an important link between chemistry (kinetics, thermodynamics) and economics (capital cost, productivity, efficiency). The key elements are interpretation of (batch) laboratory data, application of the resultant models to continuous operations, and industrial equipment selection (and costing). When successfully combined, these tools allow optimisation of the business case for both new refinery designs and brownfield upgrades.

As both computational tools and fundamental chemical understanding improve, there is opportunity for improved application of chemical reaction engineering to the Bayer process. This paper presents a brief review of the application of Chemical Reaction Engineering in the Beyer process. Predesilication design is used as an illustration.

Introduction

Chemical Reaction Engineering (CRE) is arguably the core discipline of Chemical Engineering. It is primarily concerned with reactor design, but must also be mindful of interactions with surrounding unit operations and of the overall business context. According to Levenspiel [1], it "uses information, knowledge and experience from a variety of areas – thermodynamics, chemical kinetics, fluid mechanics, heat transfer, mass transfer and economics… with the aim of properly designing a chemical reactor".

Key elements of CRE include:

- Interpretation of laboratory or pilot test data (most often "batch" data). This includes understanding of impact of process parameters (temperature, pressure, concentration, agitation rate, catalyst concentration, etc) on reaction rate and selectivity.
- Using this understanding to select appropriate reactor system (plug flow, CSTR, recycle reactor, etc) and conditions.
- Optimisation of the reactor design. This includes trade-offs between reactor costs, process performance and impacts on upstream and downstream equipment costs.

CRE and the Bayer Process

The Bayer process is a mature technology, now well into its second century. There has been steady improvement in process efficiencies, mainly through improved equipment technology, subtle flowsheet modifications and new impurity removal processes.

Despite improved economies of scale over the last 40 years, the Bayer process remains highly capital-intensive, with capital costs representing as much as 50% of full business costs for new refineries. While materials handling and heat recovery systems sometimes tend to dominate the equipment list, effective reactor design and application of CRE principles is an important tool for minimizing capital costs while maximizing process efficiency.

The key chemical reaction steps in the Bayer process have been well documented previously. The main (desirable) reactions are:

- Dissolution of alumina species (gibbsite, boehmite, diaspore) [2]
- Gibbsite crystallization [3].
- Gibbsite calcination to alumina [4].
- Preparation of filter aid [5]

In addition there are undesirable reactions and byproducts:

- Kaolin dissolution [6] followed by desilication product formation [7]
- Gibbsite and Boehmite crystallization as scale and onto residue particles [8]
- Coprecipitation of impurities with gibbsite [9]

Finally there are specific impurity removal reactions such as:

- Carbonate causticisation
- Crystallization of impurities such as sodium oxalate
- Formation of calcium precipitates of various impurities such as phosphate, fluoride, etc

The mechanisms and kinetics of the above reactions are often presented in simplified forms. Yet the reality is that there are often multiple competing reactions taking place, with heterogeneous surface impacts, multiple reaction paths and non-ideal solution behavior. Understanding of the true underlying thermodynamics and kinetics is often limited.

Within the above context, application of CRE in the industry has been mixed. There are both good and bad examples in the literature and in practice.

In general the vast majority of the published literature focuses on the impact of temperature, caustic concentration and reagent concentrations on reaction rates and equilibria. By contrast there are relatively few publications dealing with reactor design considerations. Some notable exceptions are:

- Kotte [2], whose landmark paper presents an elegant treatment of the interactions between temperature, equilibria, rates and residence time distributions on both desilication and digestion reactions
- Mugnier et al [10] who present a clear illustration of the influence of reactor type (batch vs CSTR) on nucleation

rates and hence particle size distribution of TCA filter aid.
- Rosenberg et al [11] whose work on causticisation includes the rare addition of some comments on reactor design ("*preferably, a low shear plug flow reactor...*")
- Cristol et al [12] who explore precipitator residence time distribution impacts.

Historically, simplified models applied. As better understanding and hence more sophisticated kinetics models are developed, there is more scope for CRE to deliver optimised solutions. Mathematics is more complex but computational power has increased as well.

Desilication as a CRE Example

This example explores the potential application of CRE principles on the design of predesilication reactor systems.

Background
Desilication in the Bayer process describes the conversion of reactive silica species into insoluble sodium aluminosilicates collectively known as "desilication product" or DSP. This is a relatively slow process relative to alumina extraction, and is generally the dominant factor in determining required digestion residence time and hence digester volume. However, digester vessels are usually pressure vessels and hence digestion residence time tends to be expensive. It is therefore common in refinery design to undertake the majority of the desilication reaction outside of the digesters. The most common method of achieving this is by "Predesilication", as described by Roberts in 1968 [13]. Other methods include postdesilication using DSP seed [14] or with lime [15]. There are also some novel approaches which separate the silica dissolution step from the DSP precipitation step in order to reduce caustic soda consumption [16,17,18].

Predesilication is generally carried out at close to 100C and requires 6-12 hours holding time to achieve the required degree of conversion. For a typical large refinery the required slurry holding volume is of the order of 10 000 m^3. This represents a reasonably significant capital cost. In addition, tanks are agitated or raked, scaling rates are generally high, and transfer of viscous slurry between tanks can be problematic. Therefore optimisation of predesilication tankage by using chemical reaction engineering principles represents an opportunity for savings.

Desilication kinetics are bauxite-dependent, so design of a new Predesilication facility will generally include laboratory testing of desilication kinetics. Batch experiments are usually used. However, for a refinery installation designed as a series of stirred tanks it is necessary to transform the batch kinetic results into equivalent CSTR performance.

Note that either agitated or raked reactor tanks are typically employed for predesilication. For the purpose of this study it will be assumed that the reactor tanks are well mixed.

In the following examples, it will be assumed that the design criterion for desilication is 90% conversion of silica to DSP, and that in the laboratory batch experiments 90% conversion is achieved after 12 hours. No "real" bauxite desilication data is used; synthetic curves are generated based on typical results reported in the literature.

Approach 1 – Modelling "Bulk" Kinetics

Because dissolution of reactive silica species from the bauxite is relatively rapid compared to subsequent DSP precipitation, it is often convenient to model the process as instantaneous silica dissolution, followed by kinetically-controlled DSP formation. Based on this "bulk kinetics" approach, the overall reaction is second-order with respect to silica [7] and can be described by an equation of the form:

$$-\frac{dSiO_2}{dt} = k \times [(SiO_2)_t - (SiO_2)_\infty]^2 \qquad (1)$$

Integration of this rate equation for a Batch reactor gives:

$$X = \frac{k't}{1+k't} \qquad (2)$$

Where X is the fraction of the total silica (relative to equilibrium) that has been converted to DSP, and k' = k [$(SiO_2)_0 - (SiO_2)_\infty$]

A batch desilication curve based on the above kinetics would appear as shown in Figure 1. Note that this "bulk kinetics" approach does not show the classical induction period or "S" curve for desilication. However, since it is generally the final stages of desilication which determine the required reaction time, it may be reasonable to ignore the initial transients. This will be explored in more detail later.
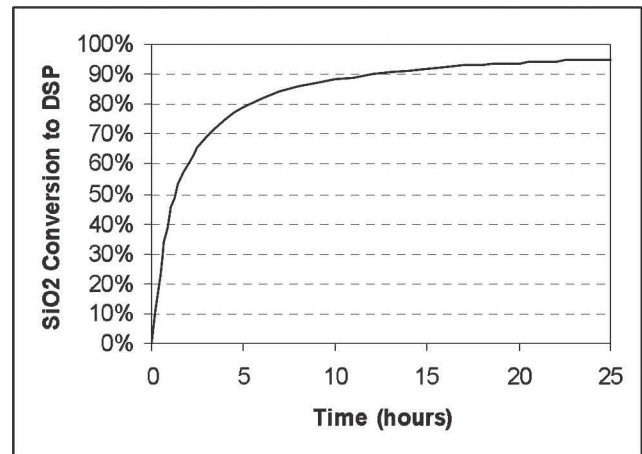

Figure 1 – Simplified Desilication Curve

Applying the kinetics from equation (1) to a series of continuous stirred-tank reactors (CSTRs), the exit conversion of each stage can be shown to be given by the following equation:

$$1 - X_N = \frac{-1 + \sqrt{1 + 4k't_N(1 - X_{N-1})}}{2k't_N} \qquad (3)$$

Where X_N is the conversion at the exit of the Nth CSTR and t_N is the mean residence time in the Nth CSTR.

Assuming, for example, 5 hours holding time per stage, the desilication curve for CSTR's in series is compared with the batch desilication curve in Figure 2. This illustrates one basic principle of CRE – that for an nth order reaction (n>0), a series of CSTR's will require a longer residence time that a batch or plug-flow reactor in order to achieve the same conversion. In this case, achieving the design criterion of 90% conversion would require four CSTR's in series. This gives 20 hours holding time, as compared to 12 hours batch holding time to achieve the same conversion.
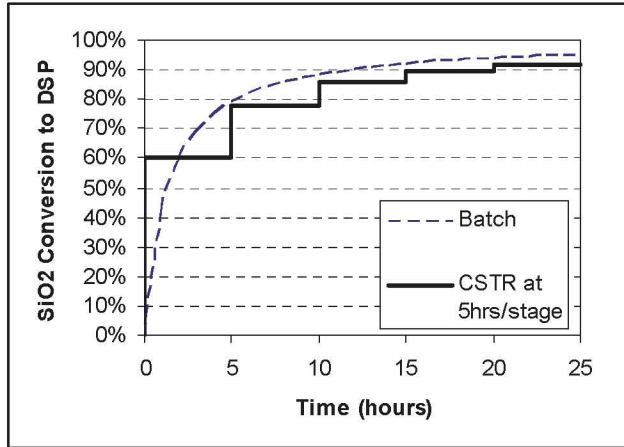

Figure 2 – Comparison of Batch and CSTR Desilication using Bulk Kinetics Approach

Of course as the holding time per stage is decreased and the number of stages is increased, the CSTR chain begins to approximate plug-flow and hence the required total residence time reduces towards that of a batch reactor. The relationship between number of stages and required residence time is shown in Table I. Note that from a total capital cost point of view, and assuming a "two-thirds power-law" approximation for scale-up of tank costs (i.e. cost per tank = a. $V^{0.667}$), minimum capital cost is achieved at N=4.

Table I – Required CSTR Volumes Based on Bulk Kinetics Approach

No. of Stages (N)	Total Residence Time Required for 90% Conversion (h)	Residence Time per Stage (h)	Total Volume Factor (relative to CSTR)
1	120	120	10.00
2	36.4	18.2	3.03
3	25.0	8.3	2.08
4	20.8	5.2	1.73
5	18.6	3.73	1.55
6	17.3	2.89	1.44
7	16.4	2.35	1.37
8	15.8	1.98	1.32
9	15.3	1.70	1.28
10	15.0	1.50	1.25
Plug-Flow	12.0	N/A	1.00

The "bulk kinetics" approach suggests that if batch results are used to directly specify required residence time for a CSTR chain, without taking back-mixing into account, then there is a risk of under-sizing equipment by as much as 40%.

Approach 2 – Seeding Considerations

The above approach ignores seeding considerations and assumes that DSP formation begins at time zero. However, it is well known that the initial DSP formation rate tends to be much lower due to the absence of DSP seed (e.g. Kotte [2]). Only after sufficient DSP has formed do the second-order kinetics used in Approach 1 begin to dominate. The result is the classic "S" curve shown in Figure 3. In such circumstances, observes Kotte, "the addition of DSP seed will improve overall reaction rate". Kotte also goes on to conclude that, at least in the initial stages of reaction, a backmixed (CSTR) reactor will give faster desilication than laboratory (batch) kinetics. This is due to internal back-mixing of seed.
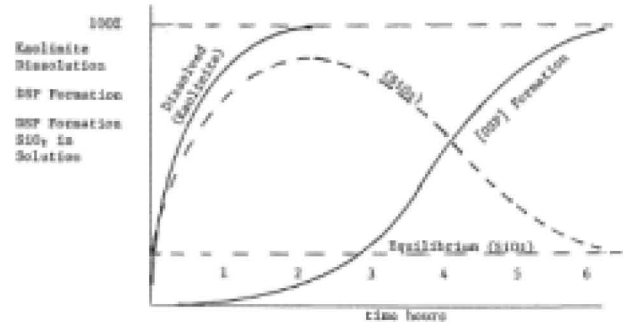

Figure 3 – Typical [Batch] Desilication Reaction Pattern (Kotte 1981 [2])

Equation (1) can be modified to reflect seeding effects as follows:

$$\frac{dX}{dt} = k'(1-X)^2(\alpha + X) \qquad (4)$$

Where α represents the amount of seed present in the starting material. Note that this initial seed does not need to be actual DSP; α may also represent the ability of other minerals present to act as seed to initiate DSP formation.

Applying these modified kinetics yields a different relationship between Batch and CSTR curves, as shown in Figure 4.
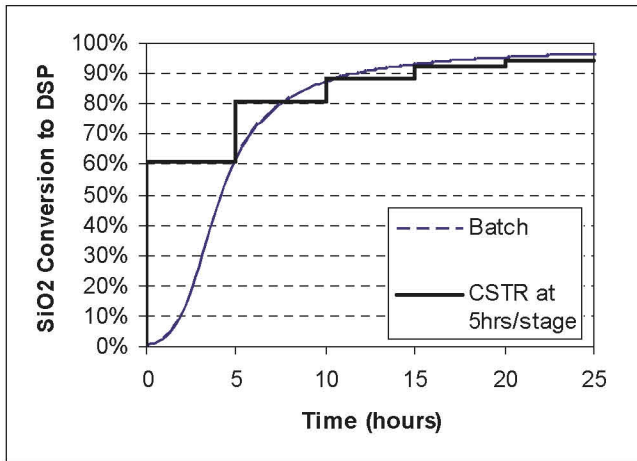
Figure 4 - Comparison of Batch and CSTR Desilication
with Seeding Considerations Included

The new relationship between number of stages and required residence time is shown in Table II below. Comparison of Table I and Table II reveals as much as 30% difference in desilication tank size (or number) depending on which approach is used to model reaction kinetics. Thus it is not sufficient to apply good CRE principles, it is also necessary to have a realistic approximation reaction kinetics and mechanism.

Table II Required CSTR Volumes Based Including
Consideration of Seeding Effects

No Stages	Total Residence Time	Residence Time per Stage	Total Volume Factor (relative to CSTR)
1	75	75	6.28
2	24.9	12.5	2.08
3	17.8	5.9	1.48
4	15.2	3.8	1.27
5	13.9	2.79	1.16
6	13.2	2.20	1.10
7	12.7	1.82	1.06
8	12.4	1.55	1.03
9	12.2	1.36	1.02
10	12.1	1.21	1.01
Plug-flow	12.0	N/A	1.00
6*	13.4	varied	1.12

*Volume of first stage doubled relative to subsequent stages

Interestingly from a capital cost point of view, 4 stages again appears to give lowest cost.

The above analysis assumes that all stages have the same volume. This is a somewhat artificial assumption and it might be reasonable to expect that a longer residence time in the first stage would provide improved seeding due to back-mixing. The final line in Table II illustrates the impact of doubling the volume of the 1st stage tank relative to subsequent stages. Despite the improved back-seeding, no net cost benefit was calculated. Thus it appears that equal-sized tanks represent the optimum configuration.

Approach 3 – PSD Considerations
The analysis in Approach 2 assumes that seeded DSP formation rate is directly proportional to the **mass** of seed. However it is more realistic to assume that the seed **external surface area** determines the rate.

Seed surface area in turn is a function of DSP particle nucleation and growth. Thus modeling of kinetics requires estimation of a nucleation rate function, and tracking of particle size distribution through the system.

In the absence of fundamental data on DSP nucleation and growth, an empirical model was developed which approximates a typical desilication curve as per Figure 3. The form of the model is:

$$B = b.[(SiO_2)_t-(SiO_2)_\infty]^4 \tag{5}$$

$$G = g.[(SiO_2)_t-(SiO_2)_\infty]^2 \tag{6}$$

The batch and CSTR desilication curves are shown in Figure 5 below.
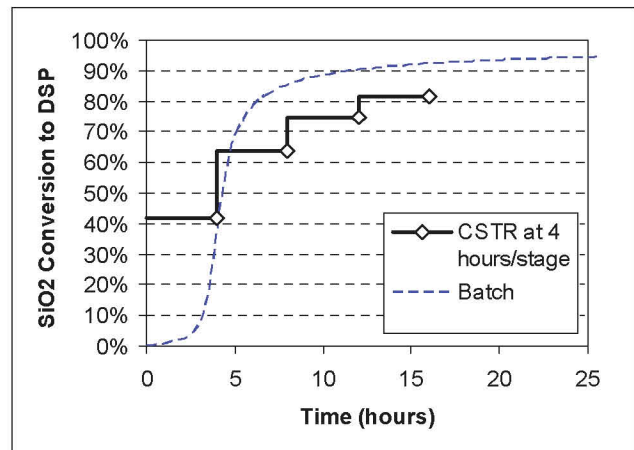

Figure 5 –Desilication Curves from PSD model

Once again the first CSTR stage out-performs the batch experiment, because back-mixing avoids the "induction period". However in this case the subsequent CSTR stages fall well below the batch curve. The reason for this becomes apparent from the DSP particle size distribution curves in Figure 6. The back-seeding and lower supersaturation in the first CSTR lead to reduced nucleation rates compared to the batch curve. This lower nucleation rate means coarser seed and hence less seed surface area in subsequent tanks.
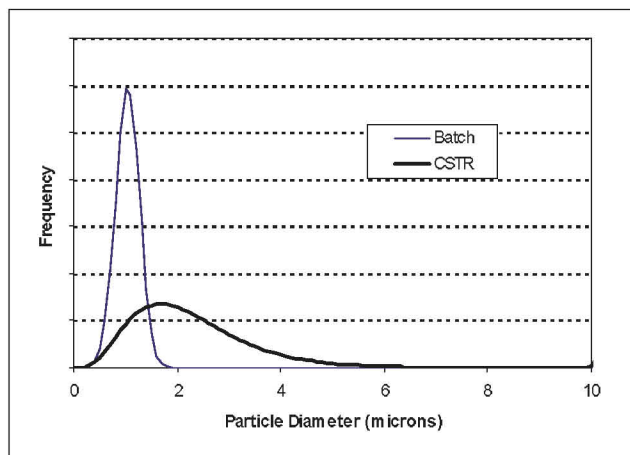
Figure 6 –Predicted Particle Size Distributions

This presents an interesting CRE challenge for the design of the first CSTR stage. There is a trade-off between backmixing (to avoid induction period) and seed generation considerations. As Table III shows, there is actually a predicted advantage in reducing the size of the first tank in order to facilitate seed generation by nucleation.

Table III. Required CSTR Volumes Based Including Consideration of Particle Size Distribution Effects

No Stages	Total Residence Time	Residence Time per Stage	Total Volume Factor (relative to CSTR)	End DSP SSA
1	275	275	22.92	0.46
2	57.4	28.7	4.78	0.75
3	33.6	11.2	2.80	0.95
4	26.8	6.7	2.23	1.03
5	24	4.8	2.00	1.11
6	22.44	3.74	1.87	1.18
7	21.98	3.14	1.83	1.23
8	22.08	2.76	1.84	1.26
Batch	12		1.00	1.44
4*	21.3	1x1.6 + 3x6.5	1.78	1.38

* First stage is ¼ volume of subsequent stages

Interestingly, the mathematical solutions for the first CSTR showed significant instability when the residence time is longer than the batch induction time. This is because high silica concentration is required to initiate nucleation, but once nucleation occurs the resultant seed surface area tends to pull down the silica concentration. A dynamic solution was not attempted but it is possible that actual operations may tend to cycle.

Discussion

The above three examples show that application of CRE principles can have significant impact on sizing of equipment. Depending on which approach is taken, the design residence time may be more than double that which is indicated by simple laboratory experiments.

The above analysis is clearly limited, in particular because it is based on synthesized curves rather than real data. There are also still some significant elements missing – for example micro-mixing (or lack thereof) is likely to play a significant role in generation of nuclei.

Nevertheless the analysis provides some directions for the designer to consider. In particular:

- Particularly close attention should be paid to the design of the first desilication tank. This should probably be a well-mixed tank of relatively low volume. Specific laboratory tests would be required to optimize this.
- Consideration of using raked tanks for subsequent stages (in preference to stirred tanks), in order to approximate plug flow. Alternatively semi-batch operation may offer some advantages.
- Be wary of possible cyclic operation due to silica build-up followed by nucleation event. If this occurs it is likely to have negative consequences in terms of both localized scaling and downstream instability.

Conclusions

Effective use of Chemical Reaction Engineering principles has significant potential contribute to Bayer plant design efficiency. There are indications that this discipline has been under-utilized in by the industry in the past. As both fundamental understanding and computational tools improve, opportunities for advanced application of CRE principles will continue to grow.

As seen in the predesilication example above, even the seemingly simple areas of the Bayer process can include complex interactions between chemistry, particle size effects and reactor design.

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