A Novel Experimental Apparatus for Red Side Studies

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Abstract

This paper presents work within Hydro's Bauxite and Alumina (B&A) R&D group to develop a novel experimental apparatus for red side laboratory scale investigations, through collaboration with the filtration company, Gaudfrin. Essentially, the equipment involves an autoclave system, capable of desilication-digestion studies, connected to a pressure filtration rig designed and produced by Gaudfrin, capable of filtration and washing studies with the autoclave product. Through operating with larger volumes than conventional lab equipment, the current set up allows for essential studies to be conducted, including new bauxite evaluation and filtration characterization. The apparatus is detailed, and some commissioning and calibration results are shown to highlight its capabilities.

Keywords: laboratory apparatus, red side, autoclave, pressure filter.

1. Introduction

Most Bayer laboratories are equipped with some sort of pressurized digestion equipment to routinely measure the relevant available alumina and reactive silica in their feed bauxite. For such routine investigations which follow standard methodologies regarding temperature, caustic concentration, residence time as well as analytical methodology for the final solution, small scale bombs with block digesters analogous to Figure 1 can be used.

This kind of apparatus does however have some limitations for non-standard test work, largely associated with the volume of slurry generated. Performing detailed kinetic studies can prove difficult, where ideally both liquor and solids analysis is performed to assist in mass balancing. For a typical small-bomb digest with say, 3 g of bauxite added, the solid residue retrievable can drop to around 1 g. To generate sufficient residue to conduct mineralogical, elemental and wet-chemical analyses, the number of bombs required increases considerably. While this can be done, running multiple bombs for the same condition in this sort of equipment can present other difficulties. For example, for a 5-minute digest, while it can be simple to extract one bomb from such an apparatus, safely removing (for example) 12 bombs, without too broad a residence time distribution, can prove quite impractical. Beyond kinetic investigations or test work requiring significant amounts of solid residue, perhaps the main drawback for Bayer Process and Bayer R&D labs is the inability to generate enough digested slurry for settling tests.

The typical settling test procedure utilizes 1000 mL of slurry, to which diluted flocculant is added and shear applied so that the settling rate and settled slurry volume can be measured (see for example [1]). Typically, at one time, five settling tests can be performed to compare the effects of variables such as flocculant dosage, solids concentration and flocculant type. While this sort of test work has its flaws and the literature points out associated misinterpretations [2], the test procedure remains a staple for both flocculant developers, researchers (see for example [3]), as well as refiners that can process different types of bauxite. As is perhaps obvious, generating 5000 mL of slurry simultaneously with the small-scale bomb digester is a practical impossibility. These considerations and the difficulties associated with the small-bomb apparatus, prompted our group to develop a larger scale digestion system.

Figure 1. a) 45 mL Parr® bomb and b) block digester for routine bauxite analysis.

When producing larger volumes of slurry, and then subsequently separating and recovering both the solid and liquid fraction, the laboratory solid-liquid separation step can prove a technical challenge. Bayer digestion residues are notorious for slow filtration using conventional vacuum equipment and conditions. This, combined with an unstable slurry associated with digestions that exceed gibbsite solubility at atmospheric temperatures, leads to an experimental difficulty. It is possible that the aluminate in liquor can precipitate as gibbsite or bayerite, preventing a functional mass balance to be achieved. While it is possible to stabilize the digested slurry using low dosages of organic reagents such as mannitol (see for example [4]), unpublished work within Hydro's laboratory has suggested that for very unstable liquor, this is still not sufficient to prevent gibbsite reversion during the filtration step. Two improvements present themselves in this situation:

1. Separate the solids using flocculants, analogous to the settling test procedure described, and filter the smaller volume of settled material.
2. Filter the slurry under higher pressure to accelerate the process.

Step 1 is routinely practiced in our laboratories, but (i) a significant amount of material is rejected in the "clear" supernatant and (ii) accurate analyses of the solid material for particle size distribution is no longer possible. These weaknesses, combined with the relatively recent developments in the industry toward pressure filtering bauxite residues (see for example [5]), prompted the pursuit of pressure filtration as part of an integrated lab apparatus. The objective was to assist with the laboratory solid-liquid separation, while allowing for measurement of filtration properties directly. Based on the widespread success of the Diastar filter [6] since its industrial inception in 1998, Gaudfrin presented as a logical company for Hydro to engage for assistance.

This paper therefore presents the developments in Hydro's B&A R&D laboratory to commission and verify applicability of an autoclave apparatus for larger scale digestion studies, as well as highlighting the joint work between Gaudfrin and Hydro to develop a pressure filter that can both operate in isolation and in conjunction with a laboratory autoclave apparatus large enough to provide the material for a range of process investigations.

2. Equipment Specifications

2.1. Autoclave System

The autoclave system currently in use in our laboratory is shown schematically in Figure 2. It consists of a 2 L autoclave (V-01) connected to a larger 7.5 L autoclave (V-02). The larger autoclave discharges through intermediate tanks (V-03 and V-04) to a sample collection bucket. Both autoclaves have electric heaters and stirrers with Parr® controllers. The small autoclave is connected to a pressurized air system, utilizing either plant air (~600 kPa) or a nitrogen bottle (nominal pressure ~1800 kPa). Both autoclaves are equipped with safety relief valves as well as rupture discs which discharge into a relief tank (V-05). While the Parr specifications put the maximum temperature and pressure of the vessels at 13.1 MPa and 350 °C respectively, the burst discs are rated for 6.9 MPa which sets a practical ceiling for their use. Procedurally, as we do not envisage utilizing the equipment at this level, any work above 275 °C or 5.5 MPa needs to be approved by the laboratory "Super-users".

Subsequent to the initial commissioning and after some operational experience, modifications were implemented to allow a separate additive solution to be transferred to the large autoclave. A 12.7 mm inner diameter tubing serpentine was fabricated and using existing tie-in points (that were capped), the additive reservoir was added. This allows for liquid solutions or very low solid concentration slurries to be added. The main function presently of this reservoir is addition of sodium silicate solutions.

2.2. Pressure Filter System

The pressure filter system is shown schematically in Figure 3. Through the installation of a T piece with valving on the discharge of V-02 (also shown in Figure 2), the slurry can discharge from the autoclave directly to the büchner, which can filter the slurry through a 2 L filter, to either a filtrate receival tank or a wash water fractioner. The wash water fractioner has been designed to allow filter cake washing tests, utilizing the wash water reservoir which is physically above the büchner. The wash water reservoir, the filtrate receival tank and the wash water fractioner can all be connected to the same plant air/nitrogen system as the autoclave. Thus, if slurry is transferred from the autoclave at temperatures above atmospheric, the pressure in the filtration apparatus can be set above the saturation pressure of the slurry to prevent against flashing. Similarly, the pressure in the filtrate receival and wash-water fractioner can be maintained above this critical pressure to prevent against flashing through the filter medium. As filtration can take

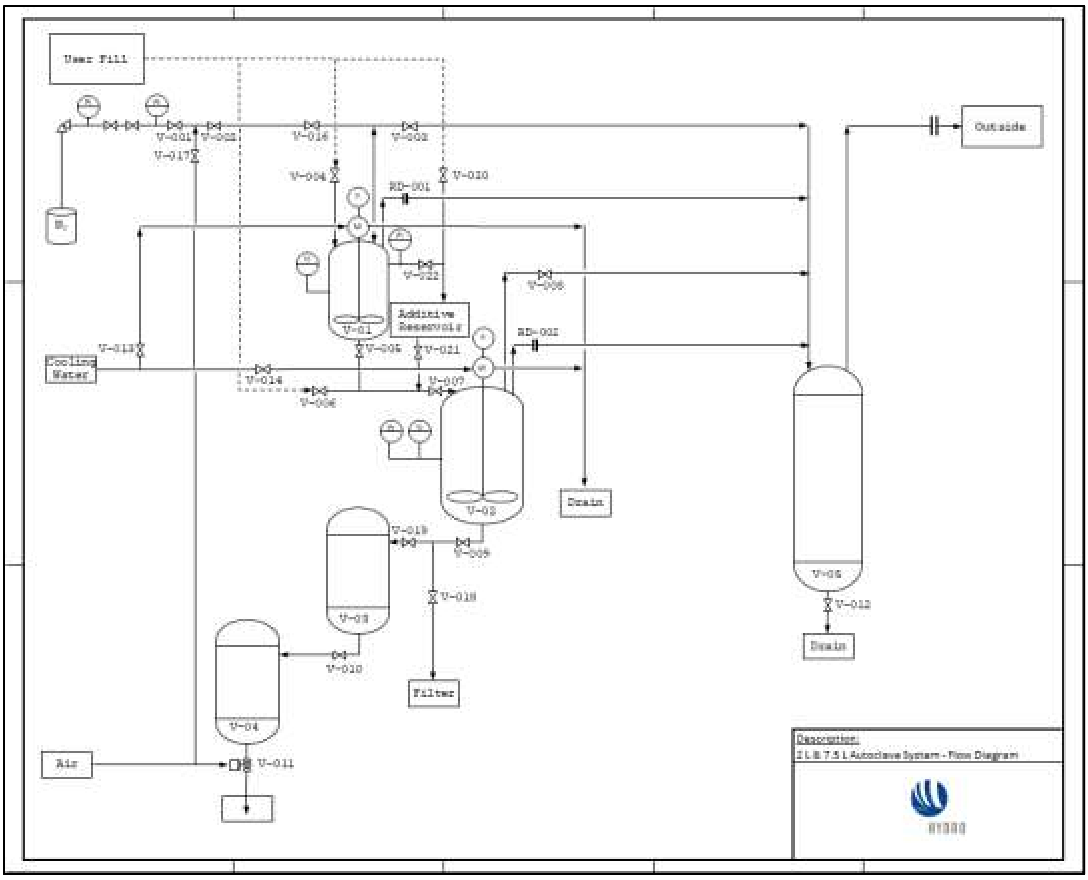

Figure 2. Rudimentary P&ID for autoclave system.

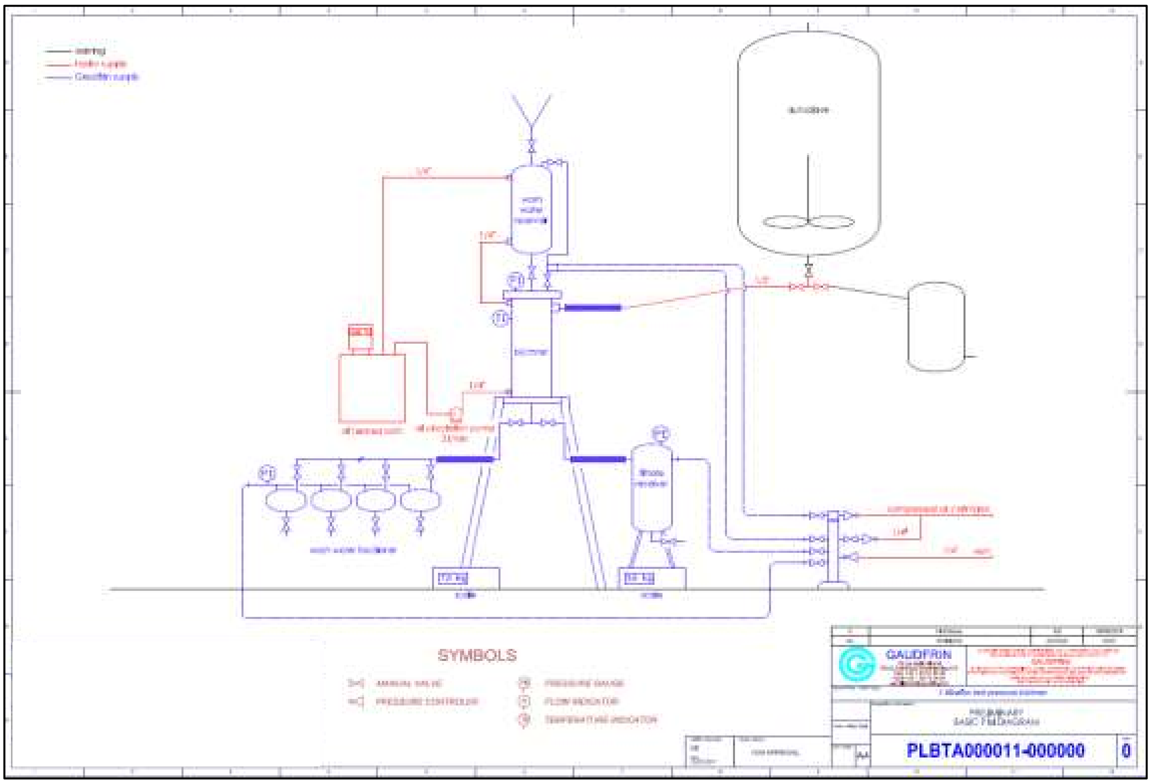

Figure 3. Rudimentary P&ID of pressure filter connected to autoclave system.

some time (even with higher pressure), in an effort to maintain a constant temperature of filtration, the büchner and wash-water reservoir are enclosed in an oil jacket which receives hot oil (Mobiltherm® 605), being heated separately in an oil bath and circulated with a small diaphragm pump. To monitor the filtration rates and manually control the flow of material from the autoclave to the büchner, balances have been placed under both the büchner and the filtrate receival tank. The balances can also act as data loggers through interface with a laptop using Microsoft Excel ®; allowing for precise evaluation of filtration rates.

3. Commissioning Results

3.1. Autoclave Commissioning

The system itself was designed and built in the early 1990s by Hydro in collaboration with Parr, but was only brought to Hydro's B&A R&D facilities in 2016, after a hiatus in usage. Based on the maximum pressure and volume of the large autoclave, the larger vessel had to go through NR13 approval which relates to safety of pressure vessels within Brazil [7]. Further to these mandatory inspections and tests, the system was commissioned through various lab procedures developed by the R&D team. These commissioning procedures were designed to confirm the safety of the vessel by gradually increasing complexity of the operation. In summary the following were conducted:

1. Air test the vessels to confirm a leak-free system.
2. Heat water in each autoclave to 150 °C, confirm leak-free system and operability of the heaters.
3. Complete a water transfer (using pressurized N_2) from the small autoclave at room temperature to the large autoclave at 150 °C to confirm the transfer capabilities of the system.

Upon success of these three basic tests, the system was deemed ready for a "real" digestion test. However, before completing a bauxite digestion test, some operational parameters needed to first be determined, namely:

1. The maximum practical bauxite slurry density in the small autoclave
2. The validity of energy balance calculations in determining the temperature set point for the large autoclave, such that the fully mixed temperature would achieve the digestion temperature target.
3. The ability of the autoclave system to generate results analogous to that achieved by bomb digestion.

To test the practical bauxite slurry solids concentration limit, bauxite-water slurries were prepared in the small autoclave and simply transferred to the sample receival bucket. The resulting slurry was filtered and the solid material collected so a percentage mass recovery could be calculated, as shown in Table 1. Based on these findings, the maximum solids loading has been set at 40 %. Further to this, for each experiment, the non-transferred solids material is collected by washing the apparatus after an experiment and filtering and weighing back this material.

Table 1. Solids recovery for different solids concentrations in small autoclave.

Solids Conc. in Small Autoclave	*Δ* Pressure (kPa)	Mass Recovery
58 %	1600	73 %
50 %	900	76 %
40 %	900	93 %

To determine the correct temperature set points in the autoclave, a basic energy balance was established. The slurry in the small autoclave is kept at room temperature prior to mixing, meaning that when it combines with the liquor in the large autoclave, the temperature drops. To guarantee a given target temperature in the large autoclave upon mixing the two streams, the temperature set point for the large autoclave (pre-mixing) is calculated using an in-house Excel® calculator which performs an energy balance. For the energy balance, the heat capacity of water, bauxite, steel and the mass of the steel are fixed parameters, while that for the liquor and the enthalpy of dissolution are taken from the literature [8]. The mass of liquor and bauxite is input by the operator, but obviously changes with the experiment being conducted. Explicitly, the following balance is performed:

$$m_{bx} \cdot c_{p,bx} \cdot T_{SA} + m_{H_2OwBx} \cdot c_{p,H_2O} \cdot T_{SA} + m_{liq} \cdot c_{p,liq} \cdot T_{LA_i} + m_{steel} \cdot c_{p,steel} \cdot T_{LA,i} = \Delta H_{rxn} \cdot m_{gibb,diss} + m_{steel} \cdot c_{p,steel} \cdot T_{LA,f} + m_{res} \cdot c_{p,Bx} \cdot T_{LA,f} + m_{liq} \cdot c_{p,liq} \cdot T_{LA,f}$$

Where:

m_{bx} is the mass of bauxite, g
$c_{p,bx}$ is the specific heat of bauxite, 0.8368 J/(g.K)
T_{SA} is the temperature in the small autoclave, 25 ^{o}C
m_{H2OwBx} is the mass of water in the small autoclave with the bauxite, g.
C_{pH2O} is the heat capacity of water, 4.18 J/(g.K)
m_{liq} is the mass of spent liquor, g
$c_{p,liq}$ is the specific heat of the liquor, calculated based on concentration, J/(g.K)
$T_{LA,i}$ is the to be determined temperature of the large autoclave prior to mixing, ^{o}C
m_{steel} is the mass of steel in the control volume, taken as 19 300 g
$c_{p,steel}$ is the specific heat of the steel, 0.502 J/(g.K)
ΔH_{rxn} is the heat of reaction taken from the literature as 385 J/g
$m_{gibb,diss}$ is the mass of gibbsite dissolved, based on a user estimated extent of reaction, g
m_{res} is the mass of residue, also based on a user estimated extent of reaction
$T_{LA,f}$ is the final temperature in the large autoclave, or rather, the temperature after mixing of the two streams.

Prior to conducting bauxite slurry plus spent liquor tests, bauxite slurry plus water tests were conducted. Excellent agreement between the target mixing temperature and measured temperature was achieved. Note that the equilibrium temperature was taken as the temperature at 120 seconds (where t = 0 is the moment that V-007 is opened to mix the streams). A typical temperature profile through time is shown in Figure 4. For the actual liquor plus bauxite-water digests, the agreement was less accurate, with a consistent difference between the set point calculated versus that observed of approximately six degrees. Based on this finding, a six-degree correction has been incorporated to the estimation procedure for the set point of the large autoclave temperature. It is assumed that this error is associated with errors in the liquor heat capacity correlations as well as the transience of the mixing and dissolution.

To understand the kinetic implications of using an autoclave which can take > 1 minute to equilibrate its temperature and transfer its slurry, conditions were compared using the bomb digesters to understand the quantitative differences. Bomb tests were completed (in triplicate) for t = 1, 3 and 5 minutes at typical digestion conditions. These conditions represent replicates of conditions tested (only once per condition) in the autoclave. In the A/TC comparison between the bomb and autoclave shown in Figure 5, it can be seen that the values are essentially the same, except for t = 1 minute. This is to be expected due to the elevated temperature achieved in the autoclave versus the bomb. It is encouraging that they are not so far removed and essentially the same beyond this time point, suggesting the two apparatus agree with one another.

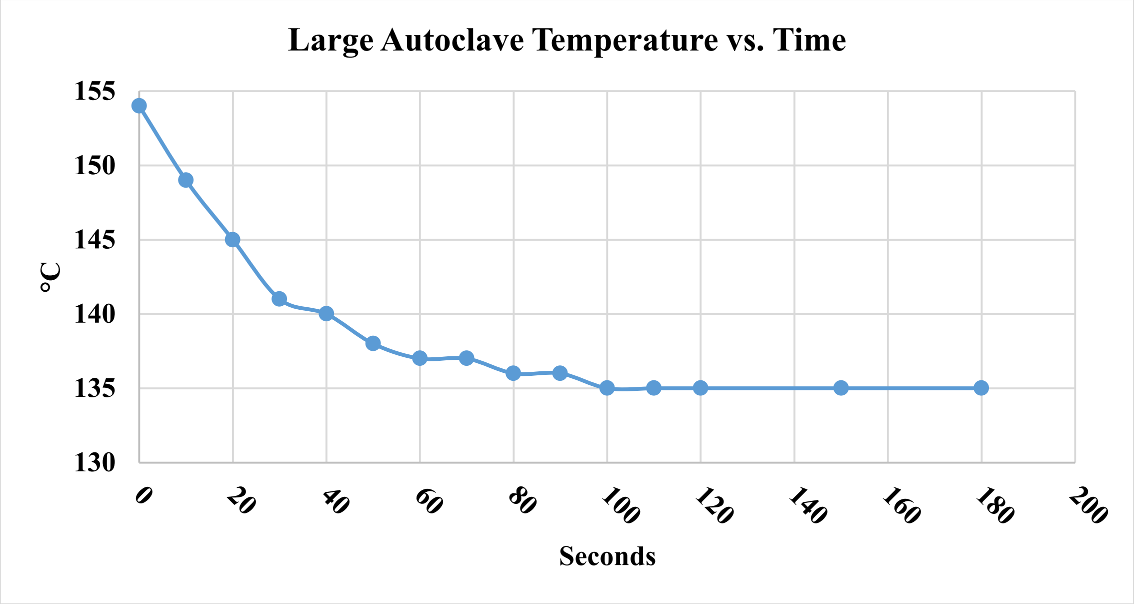

Figure 4. Temperature after discharging small autoclave contents into large autoclave.

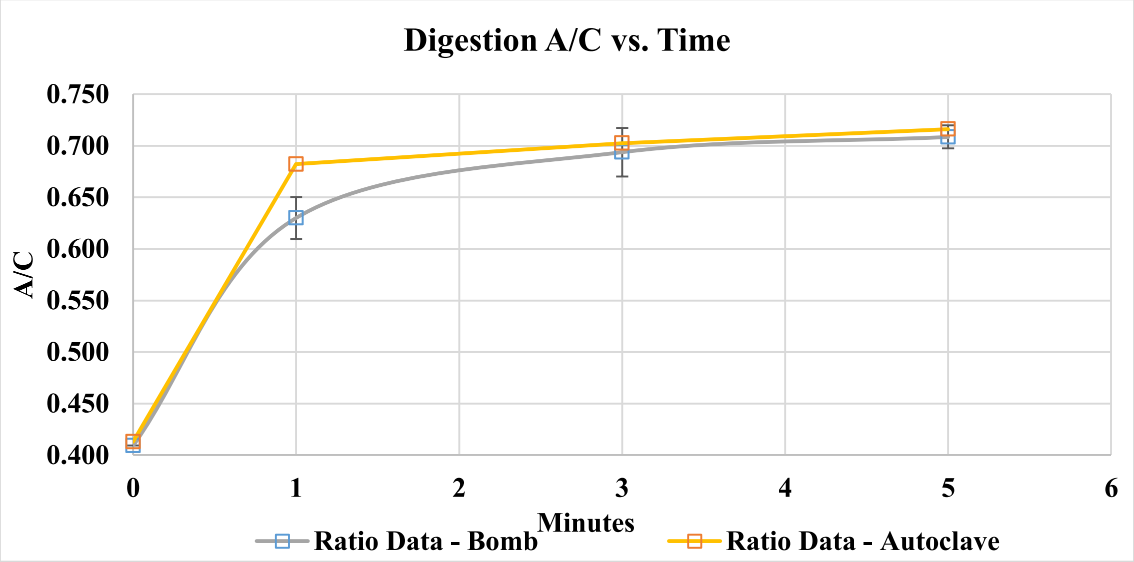

Figure 5. A/C ratio versus digestion residence time for small-bomb and autoclave system.

3.2. Pressure Filter Commissioning

The pressure filter was designed and fabricated by Gaudfrin in the second half of 2017, after discussion with Hydro R&D regarding the purpose of the equipment. Once construction and testing was completed in France, the equipment was sent to Brazil in Q4 2017. After assembling the filter within the R&D lab, each vessel (büchner, wash-water reservoir, filtrate receival tank and wash-water fractioner) was leak tested with plant air and/or nitrogen up to ~1.4 MPa. Subsequent to this, a simple water test was conducted, verifying unrestricted flow between vessels both with and without supplemental pressure. Finally, a transfer test was executed whereby 3 L of water was put into the large autoclave, heated above atmospheric boiling point and transferred to the pressurized Büchner with oil circulation at > 100 °C. Monitoring of the transfer using the balances was confirmed as a viable solution, as was the method for transferring from the autoclave to the Büchner. The material was subsequently drained to the filtrate receival tank (also at pressure), before terminating the test and relieving the excess pressure through the relief line on the gas manifold. Subsequent to these basic commissioning tests, the system was deemed ready to test with a digestion slurry from the large autoclave. A photo of the entire system showing both the autoclave and pressure filter can be seen in Figure 6.

During this testing phase of digested bauxite slurry filtration, four filter cloths were tested which were both able to withstand the temperature and caustic concentrations encountered in the filtration. For both cloths, the initial filtrate was dirty as expected, but once the initial filter cake had been deposited, the filtrate clarity improved dramatically. It was found during this initial testing phase that high pressures could not be used immediately in the filtration. In the case of initial pressure differences greater than 100 kPa, too much initial pressure pushed the solids through the cloth without giving them the chance to “bridge” over the pores of the cloth. To avoid this, the current strategy is to filter the slurry with a 100 kPa pressure difference for the first 30 seconds. Subsequent to this cake formation step, the pressure in the büchner can be adjusted. Some example filtrate mass versus filtration time experiments showing different filtration pressures can be seen in Figure 7.

Subsequent to filtration, the cake can be washed, with water pre-heated in the wash water reservoir. The wash water can be collected in the wash-water fractioner (or in the filtrate receival tank) and measured for conductivity as a simple surrogate for the caustic concentration of the liquor. An example wash curve generated from washing a filter cake is shown in Figure 8.

Figure 6. Autoclave apparatus (right) and pressure filter (left) in the B&A R&D laboratory.

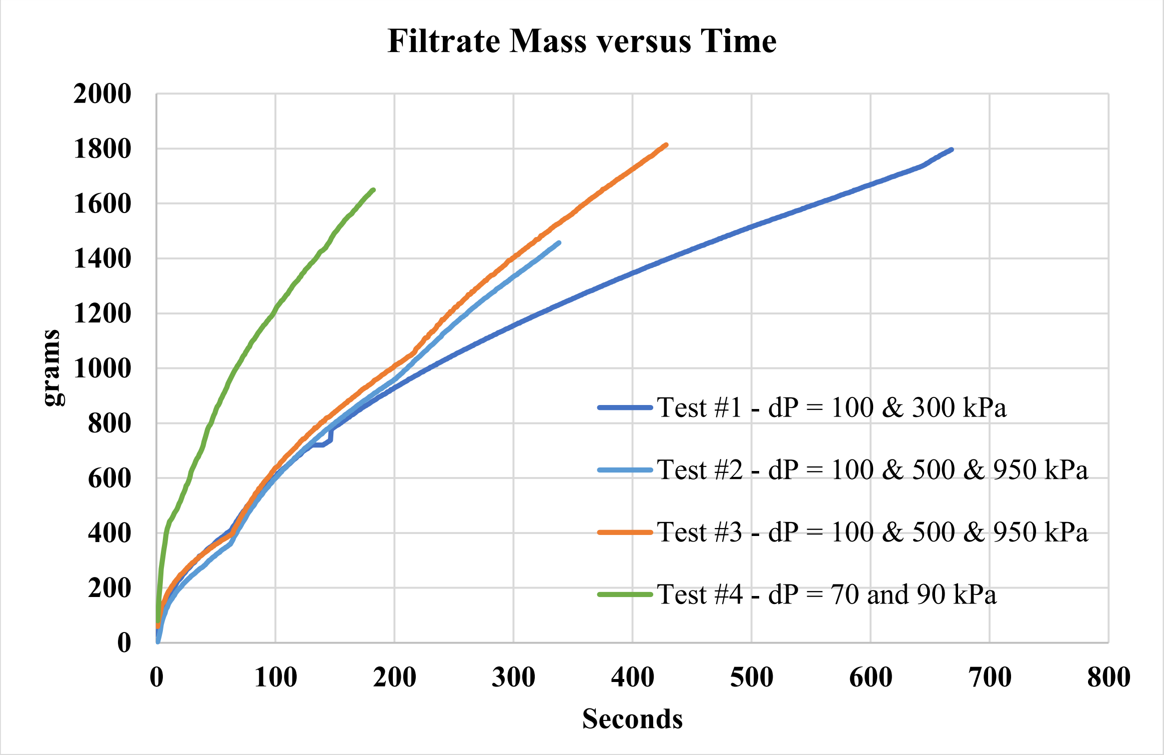

Figure 7. Example filtration rate data generated from slurry digested in autoclave and filtered in press filter.

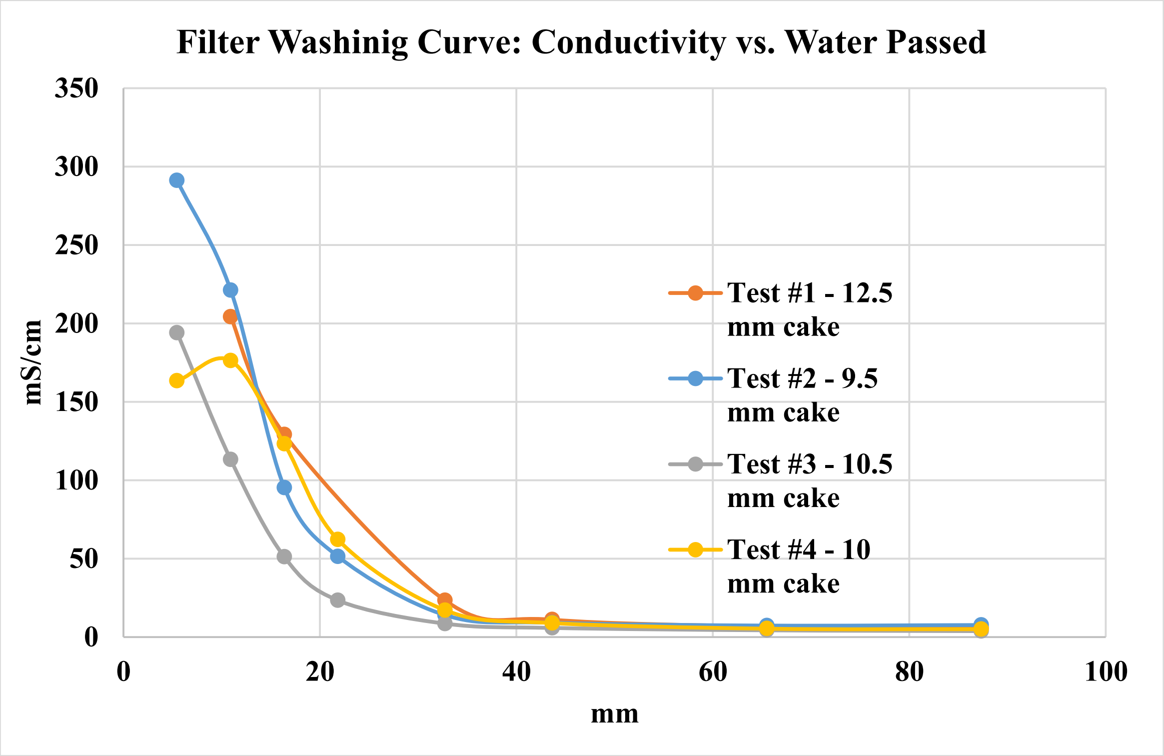

Figure 8. Example wash curve generated using the pressure filter and the filtrate receival tank. Note the units for the x-axis; 1 mm corresponds to 0.1 mL/cm². For our büchner with 108 mm diameter, 20 mm corresponds to 183 mL.

4. Conclusions and Next Steps

The safety and viability of both the autoclave and pressure filter, operating in isolation and unison has been demonstrated. Test work is now underway in various facets of both R&D projects and refinery technical support, utilizing either or both apparatus described here. After some usage, areas for improvement have been identified and will be introduced in the future. The current oil bath system for heating the pressure filter is an open system with a rather primitive manual temperature controller. To prevent the unpleasant odors and improve the safety even further, a closed system with a PI temperature controller has been designed and is under construction. A data logger for the temperature profile of the autoclave is also under consideration which would make the data recording for the experimental analysts much less onerous. Fundamental to the sustainability of the system as a whole is the preventative maintenance program to calibrate necessary equipment and replace/check different components. This program is still underway and to be finalized in the near future.

5. Acknowledgments

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