Optimization of Acid Descaling Efficiency of Bayer Process Slurry Heat Exchangers

Marc Thomas[1], Vaughn Phang[2]
1. Chemical/Process Engineer
Jamalco, Halse Hall, Clarendon, Jamaica W.I.
2. Chief Operating Officer
Paramount Jamaica, Kingston, Jamaica W.I.
Corresponding author: marc.thomas@jamalco.com

Abstract

Low temperature digestion of gibbsitic bauxite is energy intensive, depending on heat transfer across tubular heat exchangers. At Jamalco, bauxite slurry heater performance is affected by fouling due to the presence of calcium and silica species incorporating spectator particles such as boehmite, hematite and goethite. The fouling of these heat exchanger tubes reduces heat transfer coefficients, affecting the energy efficiency of the refinery. A combination of mechanical and chemical cleaning is typically done to restore the heat transfer surfaces with inhibited hydrochloric acid being the solution traditionally used. An investigation was undertaken to study bauxite slurry-based scale removal considering adjusted blending and treatment methodologies considering inhibited hydrochloric acid and its interactions with several surface-active agents. Acid solution concentration and treatment time were also evaluated to determine impact on cleaning efficacy. It was found that a revised cleaning solution formulation of inhibited hydrochloric acid and a low dosage surfactant blend improved cleaning efficacy by more than 200 %. Cleaning efficiency was found to improve through continuous monitoring of acid concentration and subsequent re-batching based on developed concentration curves, and extended acid contact time. This paper outlines the methodology used during this experiment, the outcomes, as well as future steps to be taken.

Keywords: Chemical cleaning, Heat transfer, Optimization, Surface-active agents

1. Introduction

The optimization of energy usage during the digestion of gibbsitic bauxite is a critical element of cost reduction within alumina refineries. Species inherent to the Bayer liquor and bauxite slurry influence fouling of heat transfer surfaces. It was previously reported that sodalite fouling layers as thin as 1 mm can reduce heat transfer coefficients by 77 % [1], with estimations that 80 % of energy cost associated with such fouling is due to additional energy required to re-heat process liquor to achieve target temperatures [2].

At the Clarendon Alumina Works, fouling occurs due to two predominant factors: deviation in slurry heating design from traditional Bayer process method and the reaction, precipitation, and deposition of slurry species. It is well documented that Bayer liquor and bauxite slurry are typically independently heated in shell and tube heat exchangers prior to addition to autoclaves for the completion of the digestion process. In those processes the predominant scale specie of concern is noted to be Bayer sodalite, the reaction product of sodium aluminate and soluble reactive silica [3]. Tube digestion has presented as a modern improvement to the digestion process as it utilizes the high heat transfer efficiency of the shell and tube heat exchangers to initiate digestion within the heating step [4]. Clarendon Alumina Works, utilizes a hybrid approach, wherein, caustic concentrated Bayer liquor is mixed with bauxite slurry and then introduced to shell and tube heat exchangers, progressively heating from 86 °C to 143 °C, then heated to 148.5 °C by contact steam and passed to a bank of autoclaves. While there is appreciable improvement in the liquor alumina to caustic ratios, the heater tubes are exposed to significant foulants in the form of the undigested bauxite solids (a source of particulate fouling), and the generation of Bayer sodalite from the liquor. Further, where fouling reduces heat transfer efficiency there is also a dilution (with respects to Bayer liquor caustic concentration) penalty due to the need for direct heating via contact steam downstream to achieve the required digestion temperature.

2. Nature of Fouling and Removal Methods

X-ray diffraction analysis of heater tube fouling indicates some difference in scale type across the bank of heater. For flash steam heaters (86 °C to 112 °C) the scale was found to be composed of calcite (40 %), goethite (16 %), hematite (15 %), boehmite (14 %) and gibbsite (6 %), In the case of live steam heaters (112 °C – 143 °C), the most common species were gibbsite (23 – 47 %), boehmite (26 – 45 %) and calcite (7 – 23 %). No significant quantities of Bayer sodalite were noted in either set of heaters.

Based on scale composition, corrosion-inhibited 8 % hydrochloric acid solution has been successfully utilized to chemically descale heater tubes immediately following mechanical cleaning (hydro-blasting, drilling and polishing). However, it has been suggested that use of a surface-active agent and organic acids in conjunction with a mineral acid, could improve the descaling properties of the resulting solution by improving the wetting/contact of scale surfaces with the cleaning solution, while limiting the formation barrier layers which otherwise reduce further acid – scale reaction [5] [6]. A review of methods employed in the dissolution of similar species found in well acidizing and oil field scale removal indicates widespread use of surfactants to reduce surface and / interfacial tension, modify wettability, speed clean-up, disperse additives, break emulsions and prevent the formation of sludge [7] [8].

The effectiveness of the mechanical cleaning of the tubes, particularly drilling, was found to be dependent on visual observation. As a result, there were noted occurrences of tubes not having been drilled despite being restricted as those restrictions were not detected due to their location within the long heater tubes. Additional acid would therefore be required to remove scale in these pockets. It was previously demonstrated, in line with classical reaction kinetics, that an increase in the initial acid concentration would accelerate the rate of removal of scale [2]. However, if a limit exists on the maximum acid concentration permitted (as is the case at Clarendon Alumina Works for safety), then the rate of change of the concentration can be reduced by increasing the starting volume of acid solution.

A study of parameters that influence the efficacy of chemical de-scaling of heater tubes within the digestion unit operations of the Clarendon Alumna Works was undertaken to optimize the cleaning solution formulation and treatment methodology. The results of both laboratory and field studies are presented herein

3. Methodology

Three (3) parameters were explored for the maximization of cleaning efficiency:
Total mass of acid utilized
Cleaning time
Modification of cleaning solution chemistry
Note: fouled heater tubes chosen for the experiment were sourced from live steam slurry heaters as these were identified as being more difficult to remove based on relative hardness.

3.1 Total Mass of Acid Utilized

Stoichiometry dictates proportionality between extent of tube fouling (mass of scale) and the required mass of acid to dissolve/remove it. Further, by virtue of the law of diminishing returns, there exists an acid concentration below which the time required for reaction would be unfavourable. Batched acid used in the process was noted to only utilize 60% of the available tank volume, presenting an opportunity to test higher starting volumes of cleaning solution without breaching operational safety thresholds.

Therefore, a fouled heater tube sample of known weight was setup as described in Figure 1 below to simulate process conditions. Clear tubing and wide mouth funnel were used to aid in observation of the particulates and general flow during the process. An 8 % corrosion inhibited hydrochloric acid solution was then circulated through the tube for 4 hours (chosen based on the refinery's existing chemical cleaning methodology) with acid concentration being determined every thirty (30) minutes. At the end of recirculation, the tube sample was dried in an oven at 105 °C and reweighed. A plot of acid concentration versus time was then done and analysed to determine approximate point of diminishing returns. Visual observations of tube interior following drying revealed the presence of additional scaling, indicating insufficient mass of acid was present in the initial solution for efficient removal. This confirmed that even in drilled tube a single batch of acid may be insufficient for descaling.

Figure 1. Apparatus used to simulate chemical cleaning of fouled heater tube.

Total mass of acid needed was then varied in two ways:

- By increasing the starting volume (while maintaining 8 % HCl concentration) to equate between 60 % and 90 % of batch tank utilization.
- Re-batching at point of diminishing returns as described by concentration curve.

3.2 Cleaning Time

To evaluate cleaning time, a fouled heater tube sample of known weight and internal volume was setup as described in Figure 1 to simulate process conditions. An 8 % corrosion inhibited hydrochloric acid solution was then circulated through the tube for 4 hours with acid concentration being determined every thirty (30) minutes via titration. At the end of 4 hours the tube sample was dried in an oven at 105 °C and reweighed.

Visual observations of tube interior following drying revealed the presence of additional scaling, thus treatment with an additional 8 % hydrochloric acid was done for another 4 hours (inclusive of period concentration determination as before) followed by drying and weighing. By this method it was possible to evaluate the total mass of acid required, the effectiveness of re-batching and the total time required for complete cleaning.

3.3 Modification of Cleaning Solution Chemistry

To evaluate the performance of the hydrochloric acid in the presence of surface-active agents and/organic acids, a series of solutions were prepared based on 8 % w/w hydrochloric acid, non-ionic surfactant, anionic surfactants, an organic acid, weak acid salt, silicone-based defoamer and generic all-purpose soap. Inhibitor dosage rate was kept constant at the standard value in line with performance specification. All organic additives were dosed in 1:1 ratios at very low dosages w/w % and two control samples used: inhibited hydrochloric acid and pure hydrochloric acid. Table 1 below shows the combination list for the formulations.

Table 1. Various formulations investigated for improved chemical cleaning effectiveness.

Formulation 1	8 % Inhibited hydrochloric acid, low dosage blend of glycol, an organosulfur compound and a weak acid salt.
Formulation 2	8 % Inhibited hydrochloric acid, low dosage blend of glycol and an organosulfur compound
Formulation 3	8 % Inhibited hydrochloric acid, low dosage blend of glycol and an anionic detergent
Formulation 4	8 % Inhibited hydrochloric acid, low dosage blend of glycol, an organosulfur compound and silicone-based defoamer
Formulation 5	8 % Inhibited hydrochloric acid (Control)
Formulation 6	8 % Inhibited hydrochloric acid, low dosage glycol
Formulation 7	8 % Inhibited hydrochloric acid, low dosage general-purpose soap
Formulation 8	8 % Inhibited hydrochloric acid, low dosage blend of glycol and general-purpose soap
Formulation 9	8 % Hydrochloric acid (Control #2)

Resultant solutions were used to treat fouled heater tube samples using the apparatus described in figure 1, with initial starting volumes scaled to represent 60 % of acid batch tank volume usage, and a run time of 4 hrs with acid concentration monitor every thirty (30) minutes. The mass of scale removed was then determined by comparing the initial tube mass to its final value after drying at 105 °C. The best performing formulation was then used to test the effectiveness of re-batching process to remove additional scale within tubes. The process was paused at 2 hours intervals during each batch to inspect internal tube condition to gain further insight to the mechanism of scale removal.

3.4 Field Assessment

The best performing formulation was then utilized in field trial for the chemical cleaning of slurry heaters in the digestion unit operation. Heater performance parameters of heat transfer coefficients and slurry temperature increase across each heater were then evaluated pre- and post-cleaning to determine the effectiveness of the revised formulation relative to that of the incumbent.

3.5 Corrosion Study

A lab-based corrosion study was conducted to determine if the efficacy of the corrosion inhibiter had been compromised due to the use of additives. New heater tube samples were suspended in agitated solutions of the revised formulation and uninhibited hydrochloric acid for eighty (80) hours to simulate expected exposure over one (1) year if cleaned for four (4) hours every 20 days. Testing apparatus is shown in figure 2 below.

Figure 2. Tube samples exposed to acid to determine effectiveness of inhibitor with organic additives.

4. Results and Discussion

4.1 Cleaning Solution Formulation

Figure 3 below indicates the scale removal rates per hour of treatment of the fouled heater tubes with 8% hydrochloric acid and various additives. Formulations 3, 4, and 7 performed similarly to the incumbent (Formulation 5) with only minor improvements in the case of Formulation 4 at 3.97 g/h. Formulation 8 performed better at 5.90 g/h suggesting that constituents within the general-purpose soap improved wettability and performance of the acid. This soap is known to contain organosulphur compound (different specie than used in Formulations 2 and 6, and at concentrations <10 times lower).

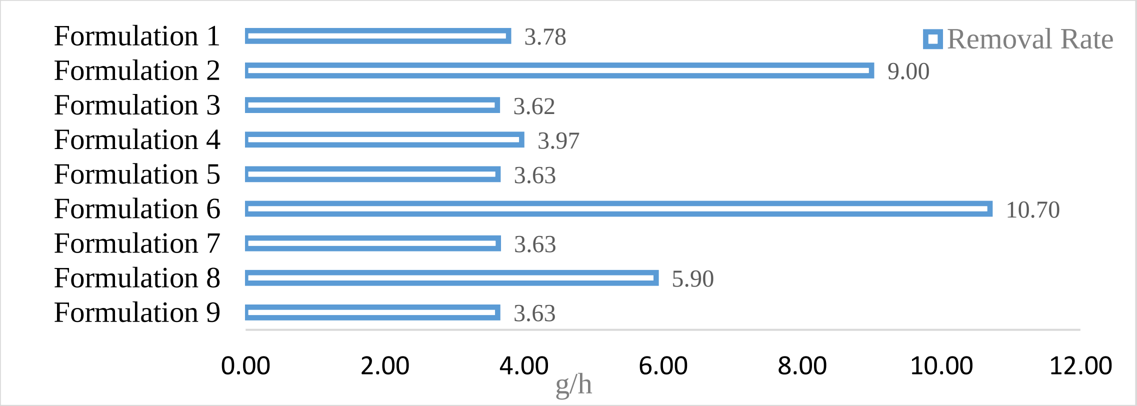

Figure 3. Scale removal rate (g/h) of various tested formulations.

Both pure hydrochloric acid and inhibited hydrochloric acid solutions yielded removal rates of 3.63 g/h. This suggest that the inhibitor does not impact the efficacy of the acid as a descaler. The combination of hydrochloric acid, organosulfur compound and weak acid salt (Formulation 1) yielded minor improvement over the base case at 3.78 g/h. However, the combination of hydrochloric acid and blend of an organosulfur compound with glycol (Formulation 2) yielded significant improvement in the solution performance resulting in 9 g/h removal, 247 % improvement over the base case. A similar result was obtained for the combination of hydrochloric acid and glycol (Formulation 6) at 10.70 g/h, 294 % improvement over the base case. While Formulation 4 differed from Formulation 2 only in terms of the use of the silicone-based deformer there was noted difference in performance. The defoamer was initially considered to reduce risk of micro-air pockets as the detergent-containing cleaning solution interacted entrained air (reduced wetting). However, its utility appears to have negated the benefits of using the glycol and an organosulfur compound as shown in the performance at 3.97 g/h versus 9.00 g/h without the defoamer.

A closer look at the remaining scale after treatment suggests that Formulation 2 softened scale layers to a greater extent than Formulation 6. To this end, it is expected that turbulent flows within the heater tubes both during acid cleaning and in the subsequent water wash cycle in the field would easily remove these weakened structures. Further, it was initially assumed that the predominant mechanism of scale removal within the tubes was via dissolution of the scale minerals in the acid. However, the process of scale exfoliation was also observed (see Figure 4a - right below). Large pieces of scale were found to be removed as thin flakes from the surface of the tubes. This mechanism suggests that large quantities of scale can be removed, provided subsequent layers can be adequately wetted (via use of the surface-active agent), contacted with acid (to dissolve any “cementing” compounds) and be agitated by turbulent flow and gas evolution (where calcite is present) within the tubes. Figures 4a and 4b below indicate changes in scale layer throughout the cleaning process.

Figure 4a. Scaled tube prior to treatment (left); evidence of scale exfoliation after 2 hrs cleaning (right).

Figure 4b. Cleaned tube following 7.5 hrs treatment including re-batching.

4.2 Field Trial of Revised Formulation

Based on the performance of Formulation 2, both in terms of mass removed and softening effect on scale, its efficacy was tested in the digestion slurry heaters, initially for a period of three (3) months but later standardized for regular use based upon results obtained. Figure 5 below presents the relative change in slurry temperature pickups across individual heaters while Figure 6 indicates the corresponding change in heat transfers. The results compare twelve (12) months preceding the trial and twelve (12) months following the start of the trial. There was no documented change in process and maintenance activities/methodologies during the period beyond the use of the new formulation.

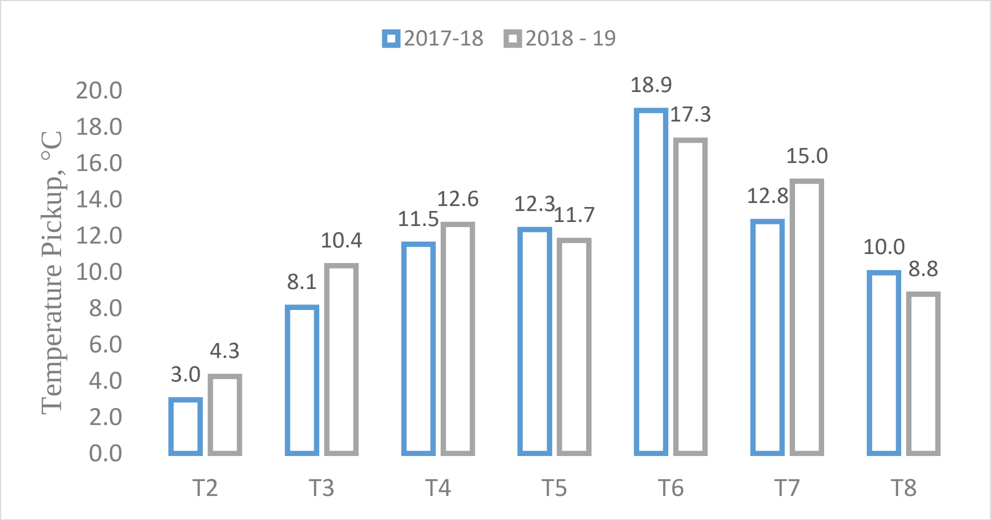

Figure 5. Slurry temperature pickups across each heater (daily averages).

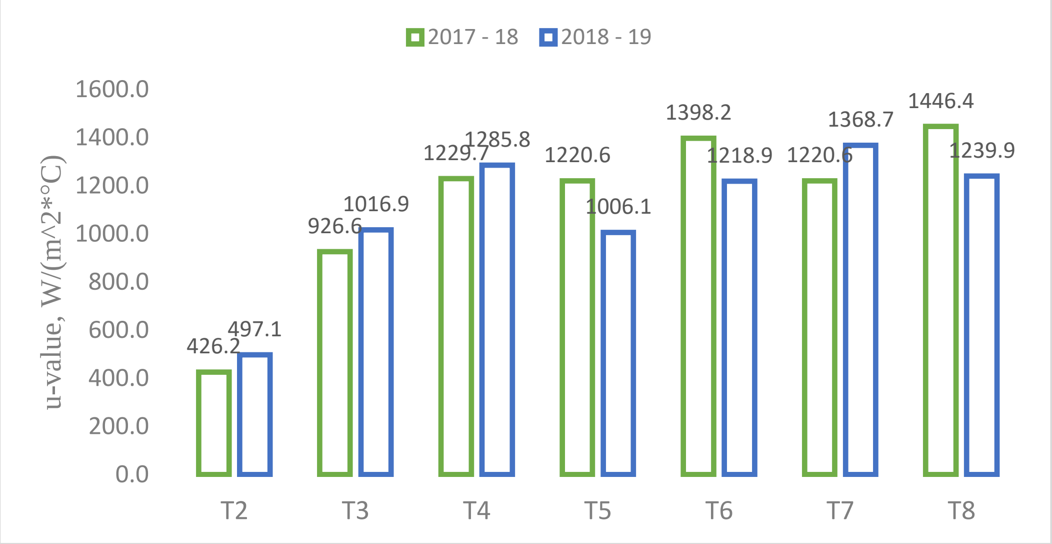

Figure 6. Heat transfer coefficients for each heater (daily averages).

Figure 5 indicates that there was an improvement in temperature pickups across four (4) of the seven (7) heaters. This resulted in a net temperature pickup across the heater bank of 62.3 °C in the twelve months following start of use of Formulation 2 versus 58.8 °C in the previous period. In the context of 2 digester banks, this improvement is significant with respects to energy consumption and reduction in dilution related caustic losses. In terms of energy cost savings, this represented more than 4 % or $US 700,000 per annum per digester unit. It should also be noted that 75 % of the improvement came from flash steam heaters, indicating improvements in energy recovery from the process. The corresponding heat transfer coefficients reported in Figure 6 support the conclusion made regarding the improvements. Both temperature pickup and heat transfer coefficient indicate an unexpected reduction in the performance of both the last stage flash heater (T5 / T6) and the last stage live steam heater (T8). While it is expected that an increase in the discharge temperature of upstream heaters would reduce the temperature gradient at the last heaters and thus reduce practical temperature pick up, further investigation is warranted. A viable starting point would be consideration around the fouling impact (scale thickness and composition) of T5 and T6 heater having the longest cycle times within the bank, some five days longer than flash steam heaters.

Opportunities remain as it relates to in-field continuous / period monitoring of acid concentration throughout the cleaning cycle, as the increased removal rates of Formulation 2 make it possible to potentially reduce clean times beyond 50 % depending on the extent of fouling present. To this end, online acid concentration monitoring is being implemented to augment existent operator-based field sampling and analysis. This system will be based on online measurement of the conductivity of the cleaning solution and correlating such to established values for percentage HCl content (calibration will be based on standard solutions of HCl doped with brine of known sodium and calcium chloride content to account for conductivity interference of reaction product species).

4.3 Acid Concentration Monitoring and Total Mass of Acid Required

In consideration of the change in acid concentration with time, results in Figure 7 below suggest that both the point of diminishing returns and time to depletion of the acid are variable. In the case of curve A, the point of diminishing returns occurs just below 6 % hydrochloric acid content with there being only 0.5 % change in concentration over the next two hours. Curve B, shows complete depletion of the acid within the 2 hours of treatment. Continuous or periodic analysis (at 30 – 60minute intervals) of the changing acid concentration should therefore be used as the guide to cleaning status and not a fixed time to completion.

This presented as an opportunity for improvement for the refinery as there has been a standard chemical cleaning time of four (4) hours despite periodic acid concentration analysis being done. In the case of curve B the rate at which the acid is consumed suggests the presence of more fouling for removal, that re-batching could address. In the case of curve A, re-batch may be needed on the basis that the scale matrix may respond better to higher acid concentrations. Care should be taken with this assumption as it is possible that the acid concentration rate of change has slowed due to unavailability of material to react with, that is, completion of the clean. Periodic monitoring of the acid concentration of re-batch solution added to the heater will indicate if reaction is continuing: if scale responds to higher concentration acid there will gradual reduction in re-batched acid concentration. If clean is complete, there would be little to no change in the batch concentration with time.

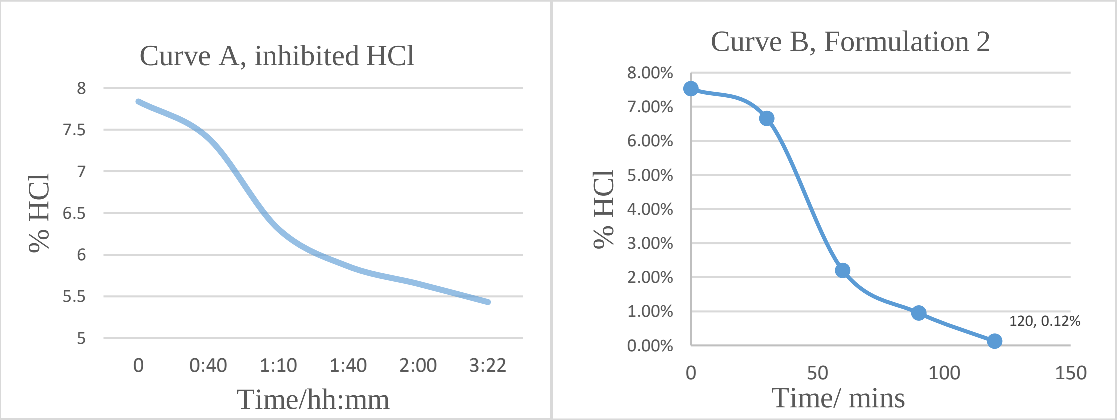

Figure 7. Concentration versus Time graphs for chemical cleaning of digestion slurry heaters

Formulation 2 was used in the determination of total mass of acid required for chemical cleaning. Figure 8 below indicates the benefits of re-batching with the result of 42 g of scale removal in 7.5 hrs such that the tube surface was cleaned to metal (see Figure 4b). In this case, the law of diminishing returns became applicable at 5.5 hour, at a concentration of 6.68 % acid. Total reacted acid was 20.8 g but total required acid for clean was 83.2 g to maintain viable concentration gradient.

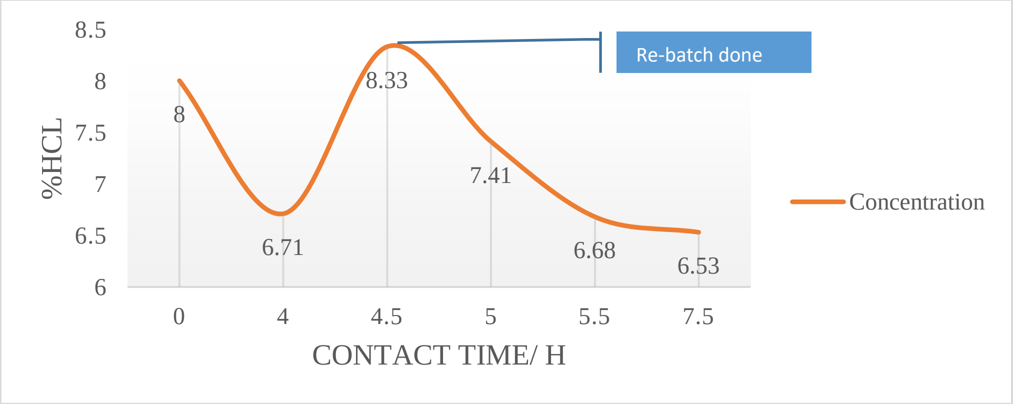

Figure 8. Effects of time and re-batching on removal.

Corrosion study results indicated a loss of only 1.5 % for tube sample treated with Formulation 2 (similar to Formulation 5) versus 4.2 % loss of mass for uninhibited hydrochloric acid. Thus, efficacy of the inhibitor has been confirmed in the presence of the additive.

5. Conclusion and Further Considerations

It was found that the effectiveness of chemical cleaning of digester slurry heaters at Clarendon Alumina Works was improved by more than 200 % through inclusion of surfactants (both anionic and non-ionic) in the cleaning solution formulation. Evidence of this was noted in improved temperature pickups across heaters, heat transfer coefficients and increase mass of scale removed. Periodic or continuous monitoring of acid concentration changes during cleaning process was confirmed to be an effective method of determining extent of cleaning and the need for additional cleaning solution to tackle heavy / difficult – to - remove fouling when compared to use of fixed cleaning time intervals.

To further improve the chemical cleaning process, the following investigations would prove useful:

- Move to field trials using 75 % capacity of batching tank
- Application of lessons learnt regarding additive use to sulfuric acid-based chemical cleaning conducted on heaters of evaporator units of the refinery.
- Investigate use of additional organic acids such as acetic acid to augment cleaning in line with suggestion in literature [6]
- Conduct further investigations into the nature of fouling at T5 and T6 heaters as well as the potential impact of the extended run cycle on type and magnitude of scale formed.
- Investigations into the benefits of sweetening existing batches with fresh acid versus complete re-batching (in terms of interaction of acid and scale with impurities from past cleans) will be critical to economic viability of the approach taken to increase available mass of acid.

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