

## **New developments in red mud flocculation and control of solid/liquid separation**

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### **Abstract**

While the Bayer process is designed to produce alumina, most operating refineries process and handle much more red mud than alumina. Thus the control and separation of red mud from liquor may be considered as the main activity of a Bayer process refinery. Efficient management and control of red mud is a critical issue in optimizing refinery operations. In addition, the focus on mud is likely to continue with good quality bauxite reserves reducing, meaning that refineries now have to process steadily poorer quality bauxite and hence will have to handle more and more red mud. Recently there have been a number of developments across a range of chemical additives that have resulted in improved capability to efficiently manage and process red mud. Key among these has been a range of improvements in flocculant design and chemistry, resulting in improved thickener and washer operations. However, products have also been developed to improve filtration processes (both for liquor polishing and red mud disposal) as well as scale control in filters, pipes and washers. Some of the opportunities that these reagents provide to improve separation, washing, handling and management of red mud are reviewed and discussed.

**Keywords:** Bayer process; red mud; flocculation; filtration; scale.

### **1. Introduction**

The focus of discussion around most alumina refineries typically centres on how much alumina the plant produces. While production of alumina is the main purpose of operating the plant, in most cases, it is not the main activity of the plant. Solid waste material or red mud that a typical Bayer plant produces and handles far exceeds the tonnes of alumina it makes. As a result, in a perverse way, alumina refineries can be considered as red mud handling facilities that produce alumina, with the main activity of the plant being the handling, separation and transport of the mud.

Estimates of global alumina production (approximately 108 million tonnes in 2014 [1]) can be used to calculate the likely global production of red mud. Based on simple assumptions of an average available alumina of 36 % and 90 % recovery, the amount of red mud processed and treated globally is estimated to be in excess of 150 million tonnes each year, or almost one and a half times the amount of alumina produced.

As a consequence, a range of chemical and engineering solutions have been developed to enhance and improve the separation, handling, treatment and processing of red mud. The purpose of this paper is to review current practice and identify new developments that may assist operators in more efficiently dealing with the increasing amounts of red mud in their plants.

Within this paper the term red mud is used in a general sense to describe all the insoluble components of bauxite that remain as solids after digestion in a Bayer plant. In this context it covers a number of species including fine clays, iron particulates and sand, as well as precipitated alumina trihydrate. It is acknowledged that some species within this broad

definition will behave differently (e.g. larger sand particles will generally settle quickly, while clay particles will not) however, for simplicity and convenience, the single term (red mud) is generally used here to describe the whole. In this context, “mud handling” can be used as a term to describe all the aspects involved in processing red mud within the circuit. This includes separation from the liquor as well as washing, transport and disposal of the solids.

Perhaps the most important step in mud handling is the separation of the solid mud from the valuable liquor. In general this is achieved by using a variety of means including thickener or settler vessels, filters, washers and residue lakes or drying ponds. While the operation and design of the overall mud handling system can significantly vary from plant to plant, the use of primary settlers for initial solid-liquid separation followed by washer vessels to recover liquor values from the settler underflow stream is very common practice across the industry. Within this process the use of flocculants to enhance settling and optimize the solid-liquid separation process in these vessels is practically universal.

## 2. Separation and washing

### 2.1 Primary settling

The primary settlers are operated to separate the bulk of the liquor from the solids. They deliver a stream of nominally clean liquor in the overflow, as well as a concentrated slurry of solids in the underflow. The efficiency of this process is effectively measured by the amount of solids reporting with the overflow liquor (which should be minimal), together with the amount of liquor in the solids stream. While it is important to minimize the liquor reporting to the underflow by maximizing the concentration of solids, the flow properties of the underflow stream must be maintained in order to sustain continuous operation. As a result, a substantial amount of liquor is required in the underflow. However, in the primary settlers, minimizing the solids in the overflow is a major operational focus.

Within any settling vessel, the dispersed red mud solids settle poorly so flocculants are used. Within the primary settlers the purpose of any flocculant is to capture and settle the mud at the required settling rate and minimize the amount of suspended solids reporting to the overflow. Historically starches were used as flocculants but the settling rates achieved using this type of chemistry was found to be generally less than desirable for modern plant operations. As a result, synthetic high molecular weight polymers are now predominantly used across the industry.

Synthetic polymers can be made from a variety of feedstocks and, in some cases the nature of the polymer can be “tailored” in the manufacturing process to deliver products with different performance characteristics.

The most commonly used synthetic polymers in the Bayer process are polyacrylate based products or polyacrylate-polyacrylamide co-polymers. The primary building block of these synthetic polymers is sodium or ammonium acrylate monomer. The acrylate monomer is either polymerized as a homopolymer or as copolymer with acrylamide (Figures 1 and 2 respectively).

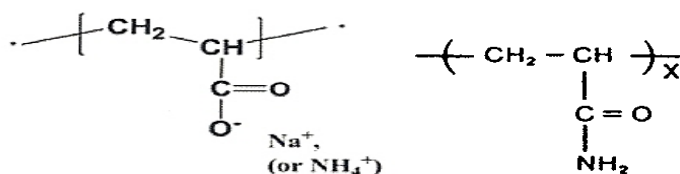
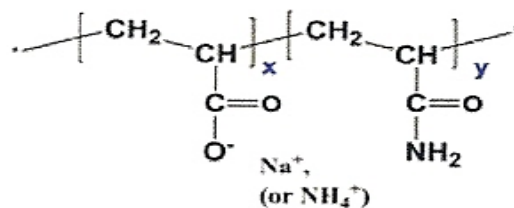


Figure 1. Structure of acrylate (left) and acrylamide homopolymers.



**Figure 2. Structure of sodium acrylate/acrylamide copolymer.**

A polyacrylate polymer is considered to be anionic in nature due to the charged acrylate functionality. A co-polymer with acrylamide and acrylate will necessarily have less charge across the backbone since the acrylamide moieties have no net charge. Depending on the ratio of acrylamide to acrylate, a given polymer can therefore have a variation in charge. In this way, flocculants can be considered to be highly anionic (e.g. 100 % charge for polyacrylate) or lower anionic (e.g. 50 % charge for a polymer containing both acrylate and acrylamide in equivalent quantities.) A polyacrylamide polymer, containing no polyacrylate, has no charge and is therefore considered to be a non-ionic polymer.

The charge of the polymer is a critical aspect of performance and under Bayer process conditions it has been shown that higher charge polymers are more effective in liquors containing high caustic concentration (e.g. primary settlers) while lower caustic slurries (e.g. last washer) are best treated with lower charged polymers [2, 3].

This type of polymer can be delivered in either a solid (powder) form or as an inverse (water in oil) emulsion or latex polymer liquid. In both forms, the products must be made up as a dilute solution prior to addition to the process. There are pros and cons for each form; powder products are more concentrated, however, they are hygroscopic and generally require specialist storage and transport equipment. On the other hand, liquid polymers can be readily pumped but generally require agitation to maintain homogeneity in the longer term and are less concentrated. On balance, both forms are used extensively across the industry and selection is generally based on site specific requirements and/or operator preference since there is generally little or no difference in the fundamental chemistry or cost performance.

In addition to the more traditional synthetic polymers, a number of variations on this basic chemical platform have been developed in the past 20 years. These variations include the hydroxamated polymers [4], polymers containing salicylic acid groups [5], or pendant siloxane groups [6] as well as the polymethacrylate based (Water Continuous) polymers [7]. In both cases the functionality of the acrylate or acrylamide portion of the synthetic polymer backbone is altered so as to deliver specific properties in application, handling or use.

More recently, red mud flocculant technology has further evolved through the modification of polymer configuration, rather than chemistry. Changes in the formulation and manufacturing process of polyacrylate polymers [8] has resulted in Rigid Rod Architecture or RRA™ polymers which have a more rigid backbone configuration resulting in less sensitivity to shear forces and superior flocculation properties. Their uptake across the industry is extensive and increasing.

Beyond this, the most recent development has involved combining the benefits of RRA technology with the hydroxamate functionality to deliver the RRX range of enhanced polymer products [9]. A hydroxamated polymer, such as RRX, can be used in combination with an RRA type product to enhance solids capture (using the hydroxamated polymer) while maximizing settling rate with minimum impact on underflow rheology using RRA [8].

In addition to the use of synthetic polymers, enhanced solids capture to further reduce mud solids reporting to the overflow (beyond that delivered by flocculant alone), may also be achieved by complementary use of natural products such as starches or polysaccharides [10,11]. Such products can be used as “clarity aids”, in addition to the flocculant. In these cases the flocculant acts as a “settling agent” in the process to remove the bulk of the solids while the clarity aid “mops up” the remaining solids. This type of combination treatment in primary settlers has gained widespread support and is now commonly practiced within the industry.

## **2.2 Mud washing**

The key driver for mud washing in Bayer process plants is the potential for substantial and costly loss of liquor associated with disposed red mud. Efficient washing, including maximizing underflow solids density in washer vessels, is a key step to minimize liquor losses and reduces the need to replace this with fresh caustic.

Washing can be done using a variety of methods but is most typically achieved through a counter current decantation circuit or deep cone vessels. In such operations the same base flocculants described above are used throughout the mud washing process.

In theory, due to the change in the caustic profile in the liquor as mud progresses down a typical counter current decantation (CCD) train, it would be possible to treat each settling vessel with a different polymer of varying charge. This would result in a product delivering optimum performance, based on the typical liquor concentration for the vessel. In practice however, the use of individual flocculants for each washing stage is impractical and typically a compromise of two or perhaps three products is employed across the entire CCD circuit. This usually involves at least one product of high charge and one of substantially lower charge.

Each individual washer can be considered as a mud handling vessel and the goal for each is the same – minimize the overflow solids and maximize the underflow solids concentration while maintaining flow characteristics of the underflow. Unlike primary settlers however, where overflow reports downstream to security filtration, the consequences of poor overflow clarity in washers are minimal since the overflow typically reports to the next settling vessel. As a result, the focus in washers is generally much more on solids underflow concentration and properties, while in primary settlers the focus more generally at the top of the vessels, on the overflow.

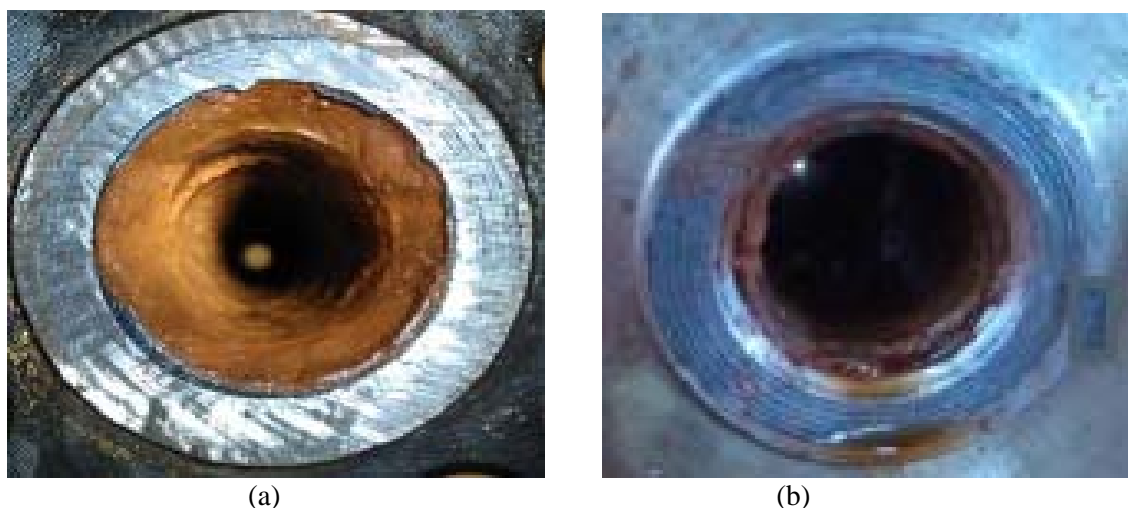
## **3. Enhancing efficiency of separation vessels**

Regardless of how well or poorly a settler or washer is operated, under typical Bayer process conditions scale will form within the vessel. Scale can grow on the sides of the vessel walls, on the rake arms and in the launders and generally consists of a combination of gibbsite precipitated from the liquor together with captured mud solids. In the worst circumstances scale deposition can result in bogging of the vessel, requiring unscheduled, off-line maintenance and remedial treatment. But even in the best circumstances removal of scale is required by regular scheduled down-time with the vessel being drained and the scale physically removed. This has a detrimental impact on overall plant capacity and mud handling efficiency.

Typically the vessel most affected by scale is the first washer where highly saturated liquor which is carried from the primary settlers with the mud is diluted to a much lower caustic concentration. This generally results in some precipitation of gibbsite – often in the form of scale within the vessels. A number of treatments have been developed to mitigate and control scale formation in settlers and washers. Most recently a new SCALE-GUARD™ product has been commercially released. The results of treatment of a first washer are shown in figure 3. The formation of scale in the overflow pipe is clearly shown following a campaign where no

SCALE-GUARD was added. This is in stark contrast to the results found over a similar period where SCALE-GUARD was used.

In one refinery SCALE-GUARD addition to a first washer resulted in extension of the on-line time from 90 days to 120 days. In addition, the descaling time was reported as shorter (faster turn-around).



**Figure 3. Images of an overflow pipe from a first washer after the same time period in separate campaigns (a) without any treatment and (b) with SCALE-GUARD addition.**

Most recently Nalco has embarked on development of products to enhance all aspects of red mud separation and handling. The outcome of this work [12] is a range of products under the RMT™ (Red Mud Treatment) banner that deliver:

- Improved overflow clarity
- Enhanced settling rate
- Improved underflow rheology

RMT products are applicable to both primary settlers and washers trains making them appropriate to deliver benefits in each mud settling and separation process.

However, it should be noted that RMT is not a replacement for conventional flocculants. While RMT can act to enhance settling of solids, it does not act as a flocculant in its own right. As a result, it can be used as an adjunct to conventional flocculants to improve settling, clarity and underflow properties and increase the efficiency and throughput of vessel operations.

The impact of RMT addition on settling rate and overflow clarity is shown in Figures 4 and 5 respectively. Laboratory result of standard cylinder tests are plotted for samples treated with flocculant alone and compared to flocculant plus RMT treatment [12].

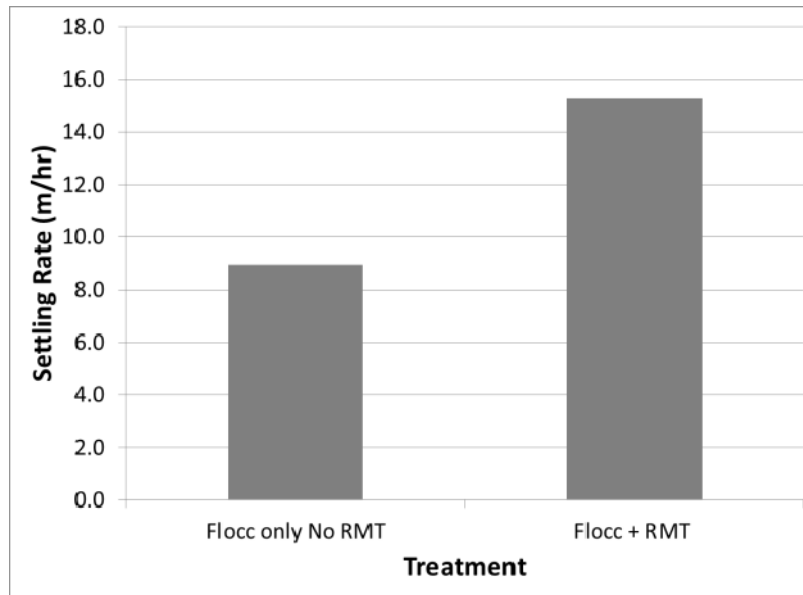


Figure 4. Plot of settling rate versus treatment for red mud. From reference [12].

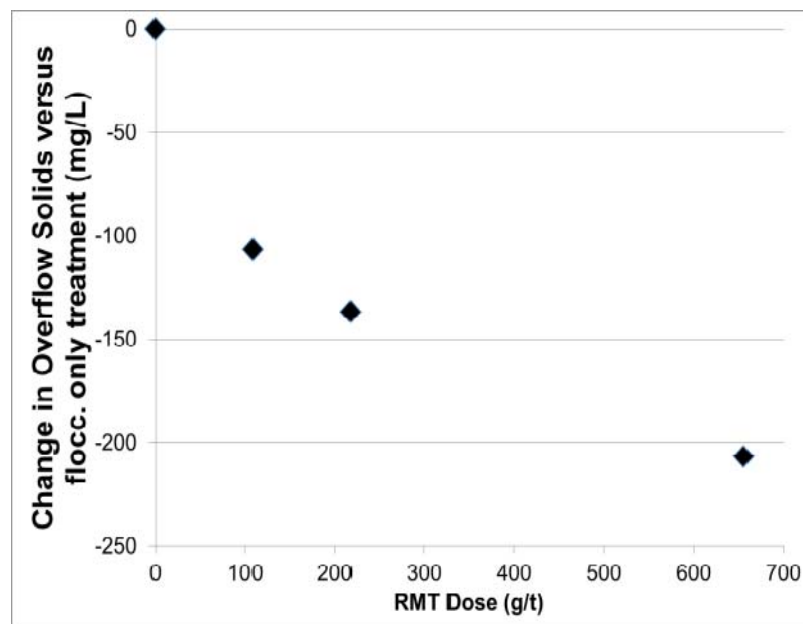


Figure 5. Laboratory data from standard settling tests using plant settler feed slurry. Standard floc dose of 22 g/t used for all points. Undosed = floc only treatment (0g/t RMT). From reference [12].

#### 4. Mud handling beyond settling vessels

While separation of mud in the primary settlers and washers is a critical process, the output streams from these vessels also contain mud and their treatment must be viewed as part of the overall mud handling process.

In the primary settlers, the overflow typically reports downstream to a security filtration step where any remaining residual solids are removed. The efficiency of this step is often critical to

the whole process since the hot supersaturated liquor must be filtered quickly to avoid both loss of alumina (which is a direct loss of product) as well as the scaling and blockage of the filter cake that such precipitation would cause. A range of products are in use throughout the industry to both enhance filtration [13, 14] prevent scale formation [15] or in many cases both.

In particular the use of SCFA™ has been shown to both enhance filtration rate by formation of a more porous cake which is less susceptible to compaction and blinding under pressure, as well as reducing alumina losses across filters through stabilization of the liquor under the conditions used for various filter types [13, 15].

From the washer stream the major output is concentrated mud slurry that is typically transported for disposal or storage. Increasingly plants are seeking to reduce the volume required for such disposal by filtering the concentrated mud slurry. Enhancing the filtration rate of this process and minimizing the residual moisture in the cake is the goal of this process and Filtermax™ products have been shown to be effective in this application [16].

## 5. Conclusion

Red mud handling involves separation, washing and transport of red mud. These activities arguably constitute the major activity within Bayer process plants and involve the use of thickener or settler vessels, filters of various types and washer vessels. A number of technologies have been developed to enhance the operation of these unit processes within Bayer plant operations. They include:

- Flocculants
  - Conventional polyacrylate-based red mud flocculants to enhance settling as well as variations of these flocculants including RRX, RRA and polymers containing functionalized groups
- Clarity Aids
  - To improve solids capture when used in conjunction with flocculants in settlers
- Scale Control Agents
  - To prevent formation of scale in settling vessels and washers
- Filtration Aids
  - Used to improve filtration rates or prevent scale, or both
- Red Mud Treatment (RMT)
  - Used to enhance solids capture and settling rate while maintaining flow properties of underflow slurry in settling vessels

Appropriate selection and implementation of products from this range of reagents allows plant operators to impact performance across a range of unit operations and optimize the red mud handling process. As a result, utilization and application of such technology can enhance the efficiency of the major activity of Bayer process plants.

## 6. References

1. International Aluminium Institute (IAI), <http://www.world-aluminium.org/statistics/alumina-production/>

2. L.J. Connelly, D.O. Owen and P.F. Richardson, "Synthetic Flocculant Technology in the Bayer Process", *Light Metals* (1986), 61-68.
3. E.C. Phillips, "New Water-Continuous Red Mud Flocculants for the Bayer Process", *Light Metals* (1999), 39-43.
4. D.P. Spitzer, A.S. Rothenberg, H.I. Heitner, M.E. Lewellyn, L.H. Laviolette, T. Foster and P.V. Avotins, "Development of new Bayer process flocculants", *Light Metals* (1991), 167-171.
5. Dai, Q., Spitzer, D., Heitner, H.I., and Chen, H.-L.T., "Use of silicon-containing polymers to improve red mud flocculation in the Bayer process", US Patent Application 2008/0257827 A1, (2008).
6. E.C. Phillips, "New Salicylic Acid Containing Red Mud Flocculants", *Light Metals* (2003), 137-143.
7. E.C. Phillips and K. O'Brien, "Development of new polyacrylate flocculants for red mud clarification", *Light Metals* (2006), 5-10.
8. D. Eckhart, J. Kildea, D. Nicholson and P. Prinsloo, "Improved Performance of Red Mud Settlers at Worsley Alumina", *Light Metals* (2010), 107-112.
9. S. Khan, "Nalco Technology Update", Australian Mining (2013)  
<http://www.miningaustralia.com.au/>
10. R. Mahoney, L. Connelly and R. Wetegrove, "Clarification Aid for the Bayer Process", US Patent 5,217,620 (1993).
11. S. Barham and J. Tippett, "Dextran Starch and Flocculant Combination for Improving Red Mud Clarification" US Patent 6,726,845 (2004).
12. R. Chester, J. Kildea and C. Urbani, "Improving Slurry Rheology: Higher Solids with Better Flow Properties for Trihydrate and Red Mud", *Proceedings of the 10<sup>th</sup> International Alumina Quality Workshop* (2015), 389-396.
13. J. Malito, "Improving the Operation of Red Mud Pressure Filters", *Light Metals* (1996) 81-86.
14. S. Barham, S. Khan, J. Malito and W. Rennick, "Optimization of Tricalcium Aluminate for Enhanced Bayer Liquor Filtration", *Light Metals*, (2000), 111-116.
15. J.D. Kildea and A. Thomas, "Scale Control and Prevention of Hydrate Precipitation in Red Mud Filters", *Light Metals* (2000), 105-110.
16. R. Chester, J. Kildea and C. Urbani, "Moisture Reduction and Enhancement of Filtration Processes for Alumina Trihydrate and Red Mud Slurries", *Proceedings of the 10<sup>th</sup> International Alumina Quality Workshop* (2015), 73-78.