

RED MUD FLOCCULANTS USED IN THE BAYER PROCESS

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Abstract

Flocculation and separation of red mud is an integral part of the Bayer process. Over the latter half of the 20th century, flocculant technology dramatically changed from natural starches to use of “rationally designed” polymers. Many of these advancements were due to the introduction of liquid or emulsion based flocculants which enabled elaborate post-reaction chemistry to be done on the polymer backbone. This paper presents a historical overview of milestones of flocculant technology used in the Bayer process up to present day. Discussion of flocculants is based on inventions in the published literature that have gained widespread use throughout the industry and will include the benefits/advantages of different flocculant technology for settling red mud.

Introduction

The Bayer process for the production of alumina has changed little since it was discovered and developed by Dr. Karl Joseph Bayer. The initial discovery (1888) that aluminum hydroxide could be precipitated by seeding a supersaturated sodium aluminate solution, and the subsequent discovery (1892) that aluminum hydroxides and oxides in bauxite could be selectively dissolved in sodium hydroxide under pressure to produce a sodium aluminate solution remain the fundamental steps in the production of alumina today [1]. Obviously, there have been tremendous advances in terms of design, engineering, and control of the process since then, but the basic operations are still based on Dr. Bayer’s discoveries.

One of the most important advances in the Bayer process has been the introduction of red mud flocculants. Interestingly, it is reported that Dr. Bayer further described the advantages of his process in terms of the purity of the alumina produced, relative to precipitation by CO₂, and the crystalline form which made it easy to wash and filter [1]. However, he also cited the main difficulty in the process was the separation and removal of the red mud; fine, insoluble, impurities that needed to be removed from the sodium aluminate solution. This is where flocculants have played an indispensable role in the process. Considering the history of flocculant use for alumina production by the Bayer process there are arguably three distinct milestones: starch, synthetic polymers, and modified synthetic polymers. Each of these flocculants have unique characteristics which is why the industry gradually moved from starch to synthetic polymers, and then to modified synthetic polymers. The benefits and performance

characteristics of each type of flocculant can ultimately be attributed to the molecular composition and also to the molecular structure. This paper examines chemistry of each type of flocculant, and correlates these differences to the flocculation performance.

Background

It is worth noting that following his discoveries, Dr. Bayer received contracts to build alumina refineries in France, Germany, Italy, the United Kingdom, and the United States [1]. Thus, it can be conjectured that the global alumina industry likely originated from the plants that Dr. Bayer helped design and build. In all likelihood the initial design of these plants did not utilize flocculants in the separation of red mud, and mud was removed by direct filtration of digested slurry. Undoubtedly, efforts at process improvement commenced in parallel among the different geographical regions where Bayer helped build refineries. However, for the purpose of this paper and the role of red mud flocculants, discussion will be limited to developments within the North American and Jamaican refineries.

In the early 20th century, there are numerous references to the use of starch as a flocculant [2-4]. The coal industry was among the first to utilize starch, in the 1930s, as a flocculant for the removal of fine coal particles from washery water [2]. Around this time, 1939, starch was also reportedly used as a flocculant to aid in the filtration of red mud [3]. It is further reported that in 1940, due to the use of lower grade bauxites in the United States, the first cone bottom settlers were installed in the process. This led to the development of counter current decantation (CCD) circuits comprised of primary settlers and washers. At this point it seems that the alumina industry was by far the largest consumer of starch based flocculants [4].

A significant advance in flocculant technology occurred in the mid-1950s with the introduction of synthetic flocculants for the mining industry [5,6]. The technical literature is rich with information on the development and use of synthetic flocculants of this era as several large chemical manufactures, in addition to governmental and academic researchers, were active in this area. These flocculants, based on acrylamide and/or acrylate offered several advantages over starch. Among these were: significantly lower dosages, higher settling rates, better filtration, improved overflow clarity, and higher underflow density. Within the North American region of the alumina industry, these synthetic flocculants were first used continuously on an industrial scale in Jamaica in the early 1970s. Synthetic

flocculants either replaced starch or were used with significantly reduced dosages of starch.

Over the years significant advancements have been made to synthetic flocculants. Many of these have been described in technical literature and include product form (solution, gel, dry powder, and oil based emulsion), molecular weight, variation in anionicity, structure, and composition. However, the most significant advancement has been the development of hydroxamated polyacrylamide (HXPAM) polymers. Development of these polymers as a flocculant was first announced in 1988 [7], and over the last 20 years they have become the primary flocculant used in red mud settlers around the world.

With above as a background, the following sections of this paper explain why the industry moved from starch to polyacrylate/polyacrylamide and then onto hydroxamated polyacrylamides. The argument presented is based on the compositional and structural differences among these polymers and the benefits they offer.

Starch

Starch is a set of natural polymeric materials primarily composed of amylose and amylopectin, and belongs to the general class of polysaccharides. It has been commonly derived from sources such as flour, corn, and potatoes. In terms of composition, amylopectin composes the outer shell of the starch grain while amylose is contained within the grain. Before starch can be used as a flocculant, a solution of it must first be made. This is accomplished through a process described as gelatinization whereby the starch grain is heated in water. During this process, the outer shell of the grain swells or expands allowing the amylose to be released. Once in solution, the amylose has flocculating properties. Amylose has an appreciable solubility in water, more so than amylopectin.

Literature on the use of starch states that the addition of caustic to the water used to create starch solutions enhanced the flocculation performance. It was conjectured that the caustic was responsible for hydrolyzing phosphoric esters, present in the amylopectin, into amylose and phosphoric acid [2]. Thus, the concentration of amylose in solution increased resulting in enhanced flocculation performance.

Structures of both amylose and amylopectin are shown in Figures 1 and 2. Structurally, both of these molecules are composed of joined glucose units. Amylose is described as more linear in its linkage configuration, a more flexible molecule, and to have molecular weights below 1 million daltons [8]. Amylopectin is a more branched molecule, and can reach higher molecular weights on the order of 10-100 million daltons [8].

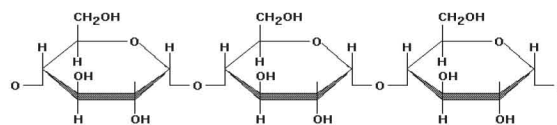


Figure 1. Structure of amylose in starch based flocculants

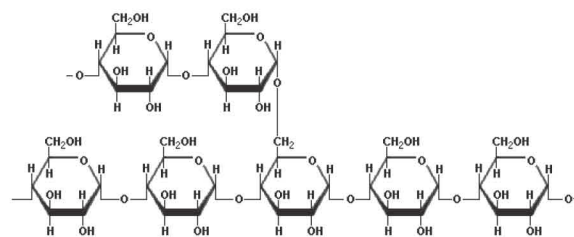


Figure 2. Structure of amylopectin found in starch.

The composition and structure of amylose and amylopectin provide insight into how starch interacts with red mud particles to form flocs. The hydroxyl groups extending from the cyclic rings are likely to adsorb on the red mud particle surface. However, because of the sterically hindered structure and the limited charge density, the starch is likely to be poorly adsorbed on the surface. More importantly, the effective molecular weight (< 1 million for amylose) is relatively low for a flocculant, and therefore there is minimal extension of the molecule from the mud particle surface to allow contact with other particles and form flocs. Floc or aggregate formation is believed to occur via a physisorption mechanism, which includes electrostatic, hydrogen and hydrophobic bonding. Although hydrogen bonding can form strong attachment of the starch to the mud particle surface, limited attachment points and molecular extension from the mud surface likely explain why such high dosages of starch are needed to effectively flocculate red mud. Dosages on the order of approximately 16 kg of starch per ton of mud solids have been reported for muds produced from some bauxites [9].

Furthermore, this would also seem to explain the significant contribution made by starch towards liquor organics concentration. Starch is very soluble in Bayer process liquor, and because of the relatively weak adsorption mechanisms; a significant portion of the dosage stays in the liquor and reports to the settler overflow. In one study, it was reported that approximately 40-50% of the total organics were due to the use of starch as a flocculant [10].

Despite the drawbacks listed above, starch is still used in a few refineries today. One positive attribute it does have is that due to its structure and size it generally does not blind red mud filter presses that are found immediately downstream of the primary red mud settlers. Furthermore, because of the high amount of residual starch in the Bayer liquor, unflocculated mud that may escape from a settler

feedwell can be flocculated in the more quiescent region of the settler before reporting to the overflow. However, despite these features, and a significant economical cost advantage, starch has essentially been replaced by synthetic polymers as the primary flocculant.

Synthetic flocculants

Synthetic polymers used as flocculants in the Bayer process are derived from acrylamide and/or acrylate monomers. Other noteworthy flocculants have been invented over the years; however the most widely used by the alumina industry have been the aforementioned. The basic structure for polyacrylamide and polyacrylate are shown in Figures 3 and 4, respectively. Furthermore, Figure 5 shows the structure of a copolymer synthesized by copolymerizing monomers of both acrylamide and acrylate. While the characteristics of these polymers have been well described in technical literature [11-15], a common feature to the structures is the flexible linear “backbone” with amide and/or carboxyl groups extending off the backbone. The linear structure enhances the aqueous solubility of the polymer, relative to highly branched polymers. This conformation is also optimal for adsorption of the polymer onto mud particles, thereby improving the flocculation performance of the polymer.

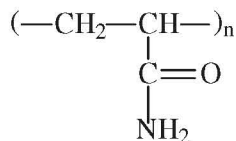


Figure 3. Basic monomer unit of a polyacrylamide.

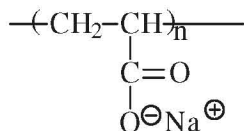
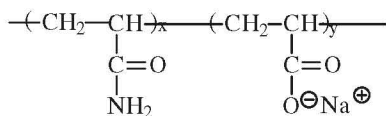


Figure 4. Basic monomer unit of polyacrylate. As shown, the sodium exists as a counter ion on the negatively charged carboxyl group.



Conventional primary flocculant, x = 5-0%, y = 95-100%

Conventional washer flocculant, x = 50-5%, y = 50-95%

Figure 5. Copolymer of acrylamide and acrylate. Respective ratios illustrate composition differences used for primary settlers and red mud washer flocculants.

As opposed to natural polymers, such as starch, there is a great deal of flexibility in manufacturing synthetic polymers. It is possible to customize the molecular weight, structure, and the amount and type of charge for a particular application. In terms of flocculation, it is quite possible to create linear polymers with molecular weights on the order of 20 million, much higher than starch or naturally occurring polymers. On the other hand, if a filter aid or dispersant is needed it is possible to reduce the molecular weight to the order of 100,000 or < 100,000, respectively. In terms of charge it is well known that primary red mud settlers require flocculants with a high degree of anionicity, such as found in polyacrylate polymers. However in middle to lower stage red mud washers, moderate (90-70%) to lower (70-50%) charged copolymers provide superior performance. Additionally, synthetic flocculants are made in a variety of product forms. Introduced initially as aqueous solutions, gel logs, or dry powders; these were the only forms until the mid to late 1970s. At this time, the invention of water-in-oil emulsion polymerizations enabled much higher molecular weight polymers to be produced in a much easier-to-use form. While dry powders are still used and offer certain benefits, the vast majority of flocculants used in the alumina industry today are inverse emulsions.

While the above information provides the compositional and structural characteristics of synthetic flocculants it does not tell the full story about why they offered such superior performance relative to starch. This is attributable to the high molecular weight and high charge density which affect how, and how much, polymer is adsorbed on mud particle surfaces. In primary red mud settlers polyacrylate is by far the most effective flocculant of the polymers discussed so far. Polyacrylate contains 100% carboxyl groups extending from the backbone of the polymer, and therefore has the highest charge density possible. The repulsive forces between adjacent carboxyl groups help extend, or open up, the conformation of the polymer in solution. This serves to increase the probability that part of the polymer will adsorb to the surface of a mud particle when a collision occurs. Adsorption of polyacrylate and copolymers of acrylamide/acrylate to the mud surface is widely believed to be through a multi-valent ion bridging mechanism whereby multi-valent ions act as a bridge between the carboxyl group on the polymer and the mud particle surface [16]. This type of mechanism would fall under a broad category of chemisorption mechanism. It is conjectured that only part of the molecule is attached to the mud particle surface and that a significant portion of the molecule extends out from the surface. The unattached portion can exist as “tails” or “loops” and serves to attach to other mud particles. Once this happens, a floc or aggregate is formed. The higher molecular weight and linear structure of synthetic flocculants is a distinct advantage in this regard. Larger flocs can be formed that have faster settling rates, and provide better mud compaction.

Perhaps the most prominent attribute of synthetic flocculants, relative to starch, is the higher settling rates achieved with significantly lower dosage. Settling rates

with synthetic flocculants were reported to be an order of magnitude higher than those achievable with starch; easily exceeding 10 m/hr. Furthermore, effective dosages were reportedly an order of magnitude less with the synthetic flocculants. The higher settling rates produced other benefits, such as increased settler throughput, and increased underflow density. Higher throughput was often an artifact of attaining higher settling rates in large settlers designed with starch as the flocculant. Increased underflow density led to improved soda and alumina recovery in the washer circuit. Interestingly, although synthetic flocculants produced higher settling rates, the flocs were more fragile than those made with starch [9, 17]. Flocs formed with synthetic flocculants were easily sheared through the underflow pumps so that additional flocculant was required in subsequent washing stages. However, the fragility was also perceived as a positive in that the flocs were more compressible and easier to dewater. Much of the “robustness” of starch formed flocs was due to small (an artifact of the low molecular weight of starch) but strong flocs, and perhaps residual starch in the entrained liquor, which acted to reflocculate the mud after the underflow pump.

The benefits of synthetic flocculants listed above far outweighed deficiencies in supernatant clarity, and filtration. While clarity was “good” with polyacrylate or various copolymers, starch was often used in conjunction with these flocculants to achieve better clarity [18]. A general performance characteristic with these flocculants was that as dosage was increased, and consequently settling rate, overflow clarity degraded [19]. This represented an operational issue in that if more flocculant was required to control mud level or increase underflow density, overflow clarity could be compromised. The solution was to supplement the synthetic flocculant dose with some starch to control clarity.

One definite drawback to synthetic flocculants that was not an issue with starch was the risk of blinding red mud pressure filters. The extremely high molecular weight of the synthetic polymers would easily blind filters if non-adsorbed, or residual, flocculant escaped the feedwell and reported to the settler overflow. A common indication of this was an immediate decrease in filter throughput, a shiny or glossy appearance of the filter cake, and a “sticky” consistency to the mud on the individual leaves of the press. Again, this difference between starch and synthetic flocculants can be attributed to not only molecular weight, but also structural differences in the molecule.

Obviously, the alumina industry has embraced the use of synthetic flocculants in the separation of red mud. This was despite a large “learning curve” associated with determining makeup and application requirements. Something normally anticipated with the introduction of new technology. As reported, the time invested in developing and converting one (of two) Jamaican refineries to synthetic flocculants easily incurred enough savings in raw materials in one year to finance conversion of both plants to synthetic flocculants [9].

Hydroxamated polyacrylamides

The latest advancement in synthetic flocculants, that gained widespread use in the alumina industry, occurred in the late 1980s with the introduction of hydroxamated polyacrylamides (HXPAMs) [20]. These polymers, as shown below in Figure 6, are an example of a terpolymer in that there are three different functional groups on the polymer backbone: amide, carboxyl, and hydroxamate. This type of polymer is only available in liquid (i.e. inverse emulsion) form and was made possible by the development of emulsion polymerization technology. It is essentially made by carrying out a post-reaction on polyacrylamide to incorporate the hydroxamate and acrylate groups on the backbone. A post reaction, meaning a separate chemical reaction after the main polymerization reaction to create the backbone, can only be carried out in any practical measure in a liquid or emulsion form. Dry powders do not lend themselves easily to additional chemical reactions, and aqueous solutions are too dilute.

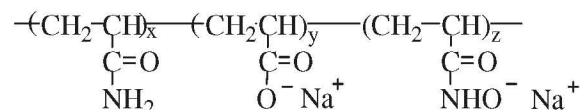


Figure 6. Hydroxamated polyacrylamide flocculant which contains three separate functional groups: amide, carboxyl, and hydroxamate.

These polymers have unique performance characteristics in that they have a positive dosage response in terms of settling rate and clarity. This means that as the dosage of an HXPAM flocculant is increased settling will increase, and clarity will also improve. This is a departure from the performance of traditional synthetic flocculants in that an increase in dosage would produce an increase in settling rate, but at the compromise of clarity. Laboratory data illustrating the different response characteristics is shown in Figure 7. In terms of settler operations, this is of tremendous value. When situations arise where higher settling rates, or higher dosage is needed the operator can make the necessary adjustment without being concerned about degrading the quality of the overflow of the settler.

Development of these types of polymers also represent the current era of flocculant research and development. The incorporation of other functional groups into traditional polymer backbones is intentional, by design, to give the polymer improved flocculation capabilities [16]. This could be improved dosage response, or the ability to flocculate selective mineralogy, such as DSP, in red mud [21].

Since the first industrial application [22] of HXPAMs in the early 1990s, these flocculants have slowly become the main flocculant used in primary red mud settlers. Initially, several refineries used these flocculants not only on the red mud settlers, but also on the washer circuit. The reason for this was the exceptional performance, and positive control

that these flocculants offered relative to conventional polyacrylate and copolymers. Since then, use of HXPAMs in washer circuits has been scaled back significantly, mainly due to economics, and the fact that copolymers deliver better mud compaction. However, a number of plants use HXPAMs on the upper stages (first or second) because of superior clarity (when the overflow goes to precipitation) and reduced auto-precipitation. Occasionally, the use of HXPAMs is extended down the washer train to deal with difficult settling mud.

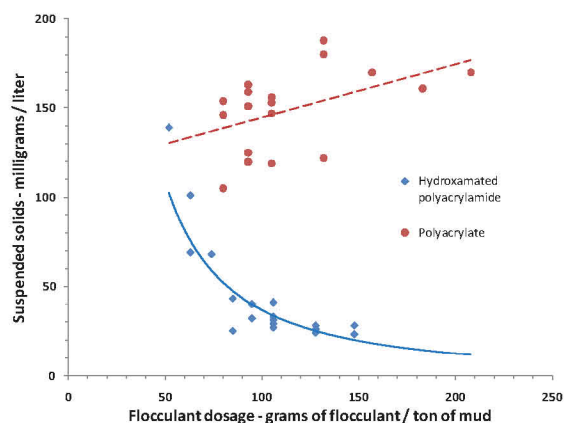


Figure 7. Supernatant clarity from lab tests showing the different responses achieved with hydroxamated polyacrylamide and traditional polyacrylate flocculants.

The unique interaction of HXPAMs with red mud particles is due to the hydroxamate functional group. This group has a very strong affinity for iron bearing minerals and tends to adsorb through a chemisorption (chelation) mechanism. Studies using atomic force microscopy (AFM) have confirmed that surface adsorption of hydroxamated polymers is stronger relative to polyacrylate [23]. Furthermore, the presence of this functional group provides faster adsorption rates for these polymers relative to polyacrylates or starch. This is particularly true in certain liquors with a high organic load. Additionally, it is what also has enabled HXPAMs to flocculate a wide range of red muds, even those considered to be difficult to settle.

As described earlier in this paper, the chief benefit of starch was the ability to settle red mud and provide a significant reduction in mud load to the filters. Synthetic flocculants brought significant increases in settling rate, settler throughput, flocculant dosage, and underflow density. Performance improvements associated with the use of HXPAMs have also been reported [24]. These are summarized in Figure 8 and include: settling of difficult mud, increased settler throughput/production, improved filtration, improved overflow clarity, and elimination of starch. Many of these improved characteristics are due to the stronger, faster polymer adsorption on mud particle surfaces. This leads to better scavenging of fine mud particles, and less residual polymer in the liquor that can blind filters. Lower suspended solids and a more distinct mud interface reduces seed sites for gibbsite scale

formation in the settler, thereby extending the life of the settler [25].

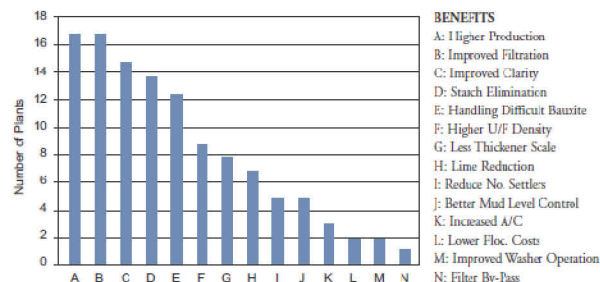


Figure 8. Summary of benefits provided by hydroxamated polyacrylamide flocculants on primary red mud settlers.

Conclusions

This paper has summarized the main types of flocculants used by the alumina industry, since the process was first discovered by Bayer. Flocculant technology was shown to have progressed from the introduction of natural polymers, such as starch, to the use of synthetic polymers based on acrylamide and/or acrylate. This led to modified synthetic polymers such as hydroxamated polyacrylamide, which are used throughout the industry on primary red mud settlers.

So what does the future likely hold for red mud flocculants? It is unlikely that there will be a change from synthetic flocculants based on acrylamide and/or acrylate in the near future. These types of polymers have clearly demonstrated the ability to provide suitable performance in the separation of red mud for approximately 40 years. Furthermore, it is difficult to compete with the economics of the raw materials used to produce these flocculants, and therefore they should continue to be the primary flocculants in the industry for the foreseeable future.

Research efforts on flocculants will likely focus on “specialty” or “rationally designed” polymers that have unique capabilities to (selectively) flocculate certain solid phase impurities, such as DSP for example. New flocculants may be utilized as a supplement to the primary acrylamide/acrylate flocculants outlined in this paper, and be used on an occasional basis. Efforts to develop this type of flocculant technology would seem to fit well with the direction that the industry is moving; processing bauxite reserves with deteriorating quality. The ability to separate and remove mud produced from these bauxites, and maintain industry specifications for alumina quality, may rely heavily on the use of processing aids, such as new flocculants.

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