Importance of synthetic flocculants in alumina industry

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ABSTRACT

In the Bayer's process of alumina production, separation of mud residue from the liquor plays an important role. Throughout Alumina production process additives are used at one stage or the other, flocculant being one of the additives. Till 70's natural flocculants were used in the operations. Starch, guar gum, wheat bran etc. were used for the purpose of settling of red mud and to attain increased solid/liquid separation rates. Slowly transformation has taken place from natural flocculants to synthetic flocculants for a variety of advantages such as improved settling rates, improved liquor throughput, high underflow consistency, improved liquor filterability, reduced organic load etc. They also control the physical and chemical properties of the Bayer process streams during the operation. Synthetic flocculants are polymers of acrylamide & polyacrylate etc. the molecular structure of which is an important factor to obtain the desired flocculation effect in the process liquors. Depending on the Bauxite quality and the process technology adopted the selection of flocculant varies from plant to plant. This paper deals with different types of synthetic flocculants available, their usage in Alumina industry.

Key words: Flocculation, Synthetic flocculants, Solid/liquid separation, Red mud

HISTORY OF SYNTHETIC FLOCCULANTS

Bauxite was discovered in Southern France in 1821 and subsequently in 1888 the Bayer's process fundamentally remained unchanged but modifications in the operating parameters, the operating equipment, use of additives have paved way to reduce the cost of production, improved efficiency, decreased raw material consumptions etc. In the Bayer's process of Alumina production settling/washing operation is considered to be one of the important unit operation. Here the
separation of mud residue from the liquor plays an important role. For this purpose starch was being used to increase the sedimentation rates and to reduce the amount of insoluble material in the feed to the filters. During the 1960’s synthetic polymers slowly emerged into the field for effective solid - liquid separation. Most of the alumina plants world over have switched over to either fully to use synthetic flocculants or with the combination of starch to provide improved clarity in the overflow liquor feeding to kelly filters and ultimately to precipitation. The changed over from natural flocculants to synthetic flocculants have variety of advantages such as improved settling rates, improved liquor throughput, high underflow consistency, reduced organic load etc. They also control the physical and chemical properties of the Bayer process streams during the operation. Depending on the Bauxite quality and the process technology adopted the selection of flocculant varies from plant to plant. Acrylate, Acrylamide, Hydroxamate polymers are the most widely used red mud synthetic flocculants. Now the latest addition to the group is the water - continuous flocculants.

CHEMISTRY OF SYNTHETIC FLOCCULANTS

Acrylic acid and Acrylamide produce water soluble polymers and both undergo polymerisation with relative ease. Both these monomers have functional groups (amide carboxylate) which are capable of adsorption onto mineral surfaces.

<table>
<thead>
<tr>
<th>a) Sodium polyacrylate</th>
<th>b) Acrylamide and Sodium acrylate</th>
<th>c) Acrylamide homopolymer:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₂-CH)ₓ</td>
<td>(CH₂-CH)ᵧ</td>
<td>(CH₂-CH)ₓ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C = O</td>
<td>C=O</td>
<td>C=O</td>
</tr>
<tr>
<td>Na(+)</td>
<td></td>
<td>Oe Na⁺</td>
</tr>
<tr>
<td>O e</td>
<td>NH₂</td>
<td></td>
</tr>
</tbody>
</table>

Cationic polymer: A polymer containing positively charged ionised group covalently bonded to the polymer.
Anionic polymer: A polymer containing negatively charged ionised group covalently bonded to the polymer.

Non-ionic polymer: A polymer containing no group capable of ionising such as polyacrylamide.

Acrylate/ Acrylamide copolymers may be categorised generally according to their anionicity as follows:

<table>
<thead>
<tr>
<th>Relative Anionicity</th>
<th>% Acrylic acid</th>
<th>% Acrylamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic</td>
<td>0-2</td>
<td>98-100</td>
</tr>
<tr>
<td>Slightly anionic</td>
<td>2-20</td>
<td>80-98</td>
</tr>
<tr>
<td>Moderately anionic</td>
<td>20-40</td>
<td>60-80</td>
</tr>
<tr>
<td>Moderate - high anionic</td>
<td>40-70</td>
<td>30-60</td>
</tr>
<tr>
<td>Highly anionic</td>
<td>70-100</td>
<td>0-30</td>
</tr>
</tbody>
</table>

The reaction mechanism through which the polymers and copolymers are formed is more or less same but the action of each flocculant differs from one another. Both acrylamide and acrylic acid undergoes the chain growth polymerisation involving kinetic chain reaction namely (1) an initiation step which can involve more than one reaction (2) a propagation step which involves a sequential repetition of identical reactions (3) a termination step wherein the chain reaction stops.

High molecular weight polymers result if the propagation step is favoured to a greater extent than the termination step. If the propagation step is not favoured to a large extent over the termination step, low molecular weight polymer results. HXPAM’s have considerable flexibility in manufacture to achieve the modifications required in molecular weights. More over HXPAM’s in Bayer liquor do not require calcium bridging as the bonding to the mud particle achieved is as shown below:

\[ (-\text{CH}_2 - \text{CH}-)z + X^+ \rightarrow (-\text{CH}_2 - \text{CH}-)z \]

\[ C = O \quad \| \quad C = O \]
\[ \| \quad \| \]
\[ \text{NH} \quad \text{NH} - \text{O} \]

\[ O \]
Water continuous flocculants are true dispersions containing small amounts of surfactant to stabilise individual, insoluble polymer particles in water. The polymer chemistry and unique solution properties provide for improvements in liquor clarification performance compared to poly-acrylate flocculants.

FLOCCULATION MECHANISM

Flocculation occurs through a bridging mechanism in which the polymer attaches to two or more particles thereby becoming a long chain molecule. Flocculants actually interact extensively with each other and function as large molecular networks in solution. Vanderwaal's forces, Hydrogen bonding and ionic bonding effects the bonding of flocculant molecules to mud particles. This bridging helps in unification of a number of small sized dispersed particles. Increasing the effective particle size of the solid phase enhances the efficiency of solid-liquid separation.

FACTORS INFLUENCING FLOCCULANT'S CHOICE

The flocculants used in mining industry range from 100% acrylamide to 100% acrylic acid.

The common combinations are:

a) 10 - 20% polyacrylamide (100% non-ionic)

b) 60 - 80% anionic co-polymer

c) 10 - 20% poly acrylate (100% anionic)

In general a polymer must have molecular weight of 300 to 4,00,000 in order to have flocculant activity. Most commercial flocculants have molecular weight above 1,00,000.

The aqueous environment has significant influence on the surface chemistry of solids being separated. Other factors influencing the performance are the particle size distribution, chemical nature of the solids, % solids in the slurry, application need etc.

The primary function of acrylamide group in copolymer is adsorption (building strong floccs) by hydrogen bonding. The primary function of the carboxylate group is to extend the polymer chain in solution by electrostatic repulsion enabling bridging to take place more easily.

High level of electrolyte can have deleterious effects on the activity of anionic flocculants, the presence of low level of cation such as calcium can result in a marked improvement in flocculant activity.
The solution PH also changes both the flocculant chemistry and rheology as well as affects the surface chemistry of the mineral particle. At a high PH acrylamide will hydrolyse to acrylate while at low PH acrylate is in chemical equilibrium with the acid form. This effects the polymer rheology.

Polymer concentration, split addition, molecular weight of flocculant has significant influence on the performance of flocculant.

Choosing the right flocculant for a given application depends on the water chemistry to a great extent. In Bayer’s process the caustic level found in settlers necessitates the use of highly anionic polymers. Since each plant is different, it necessitates a preliminary laboratory screening test to select the right type of flocculant as well as the method of addition.

**SELECTION OF FLOCCULANT**

In general every mud has its own nature and characteristics and in many cases the flocculant is tailor made to suit the requirement of the specific residue. Selection of a suitable flocculant is required to get a good overflow clarity, high settling rates, improved U/F consistency. Conventional jar settling tests are to be carried out to select a suitable grade and to optimise the dosage, points of addition etc.

Once the lab trials establishes various parameters and operating conditions plant scale trial needs to be done. Better mud compaction can be achieved by increasing the U/F solid consistency which in turn will reduce the soda losses through mud. Acrylate and hydroxamate flocculants goes well with settlers whereas acrylate/ acrylicamide suits well for washing circuit.

**ADVANTAGES OF SYNTHETIC FLOCCULANTS**

Synthetic flocculants have varied advantages over natural flocculants. These are given below:

1) Better overflow clarity thereby reducing the suspended particulate matter to the pregnant liquor.
2) Improves the liquor filtration so that more throughput is achieved.
3) Prevents gibbsite scale formation.
4) Reduce auto precipitation.
5) Improve hydrate classification.
6) High settling rates.
7) Improve underflow consistency of mud.
8) Reduced soluble soda losses with mud.
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In case of water - continuous flocculants the additional benefits are that organics to the process, easier to pump and store, remains intact on long standing. The low bulk viscosities provide for easier handling. Spill overs can be easily cleaned. Hence safe to handle.

In case of HXPAM’s they have the impact on thickner life as well as on consumption of lime.

CONCLUSION

Synthetic Flocculants provide effective solution for better solid - liquid separation. They reduce the organic input to the process streams, increases the settling rate, reduces the specific capital and operating costs etc. Its use will result in optimised equipment sizing for expansion as also the operating efficiency of the existing equipment increases.

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