

The Impact of Organic Additives on Phase Transformation and Particle Size of Bayer Process Desilication Product

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Abstract

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Organic additives are used to tune the morphology and particle size of crystals in the zeolite manufacturing industry. However, their impact on phase transformation and size distribution of desilication product (DSP, belonging to the zeolite family) in Bayer desilication has not yet been extensively studied. In order to probe this impact, crystallisation of DSP in the presence of fifteen organic additives was studied in a batch reactor using synthetic solution. The results indicate that certain additives effect the phase transformation of zeolite A to sodalite and the particle size distribution of DSP produced. Solids samples were characterized using x-ray diffraction, scanning electron microscopy and their particle size distributions were measured using an AccuSizer particle counter.

Keywords: Organic additives, desilication product, crystallization, Bayer process.

1. Introduction

Reactive silica in bauxite, predominantly in the form of kaolinite and quartz, react in the Bayer process, driving silicate into solution. Once a critical supersaturation is reached, this silicate combines with other aqueous species to re-precipitate in the form of sodium aluminosilicates or zeolites known as desilication product (DSP). DSP precipitation, referred to as desilication, reduces silicate levels in process liquor, preventing silica contamination of gibbsite product, and is therefore an important step in the Bayer process. However, DSP can form unwanted scale, and also consumes valuable caustic and aluminium which exit the Bayer cycle as residue along with other minerals.

Bayer DSP types found in industry are predominantly in the form of sodalite and cancrinite [1]. However, these are known to form through a series of solution mediated phase transformations. These metastable transformations begin with an amorphous sodium aluminosilicate phase which converts to zeolite A, then to sodalite and then to cancrinite [2]. Desilication can occur in pre-desilication or digestion, depending on the configuration and reaction conditions of the Bayer plant. In synthetic solutions where silicate is introduced as aqueous Na_2SiO_3 , at pre-desilication conditions (90 °C) as in this study, these transformations are slower and phase transformations can be clearly differentiated.

DSP precipitation control through the use of additives has been investigated to predominantly control scale formation. Commercial additives exist which have proven to reduce scaling by modifying liquor solubility properties [3, 4]. The Bayer process has also employed organic additives in the form of crystal growth modifiers (CGMs) to improve gibbsite precipitate properties for example to increase crystal size, reduce fines and to improve yield [5]. Modifying Bayer DSP crystal morphology through the use of CGMs has not yet been extensively investigated.

The research into modification and synthesis of various types of zeolites for industrial use, has a long history. This is due to their many varied and valuable chemical properties which are predominantly determined by their morphology. These properties are utilized in a number of industries including petrochemicals and detergents and include; ion-exchange ability, sorption capacity, shape selectivity and catalytic activity [6].

Through this research a number of additives have been shown to impact the crystallization of zeolites. Zeolites are typically synthesized in a strong basic medium which assists in the mineralization of silicate and aluminate species in reactant gels [7]. Organic structure-directing agents and seed assisted synthesis of zeolites are commonly employed to direct their formation, for example to stabilize the framework of zeolite molecular sieves [8]. Synthesis methods of various zeolite types have been historically patented, for example that of large zeolite crystals (up to 100 μm) through gel crystallization using an organic nitrogen compound additive [9]. In zeolite manufacturing, cations have been shown to influence anionic species present in solution and dissolved quaternary organic ammonium bases (such as tetraethyl ammonium bromide, TEAB) have been used as charge compensating cations in zeolite synthesis to modify morphology from as early as 1961 [10]. These organic compounds could have a significant impact on Bayer DSP and could be explored as pre-desilication additives to change DSP morphology.

Predicting the effect of modifying additives on crystal growth and morphology however, has proven to be difficult [11]. The range of organic additives chosen for this study was therefore kept broad to encompass common surfactants, polymers/flocculating agents, known Bayer impurities, organic acids, commercial reagents and zeolite CGMs. Myatt et al. tested a number of surfactants including sodium dodecyl sulfate (SDS), sodium dioctyl sulfosuccinate (DSS), cetyltrimethylammonium bromide (CTAB) and polyethylene glycol (PEG), observing the impact of these on zeolite A crystallisation [12]. These additives were found to increase the linear rate of crystal growth and sodium dioctyl sulfosuccinate was shown to reduce the number of nuclei produced. Sanhoob et al. investigated the effects of PEG on the pore structure of zeolite ZSM-12 and found that it played a significant role in controlling crystallization rate [13]. A medium size polyacrylic acid molecule (5200 MW) was also chosen, as this has shown to be effective in modifying oxalate crystal structure in previous studies under Bayer conditions [14].

2. Method

Initially, 12 additives were trialed as part of a scoping study and these are listed in Table 1. All were initially tested at 100 mg/L in batch stirred reactor tests. Cytec – Cyphos ionic liquid (IL) 101 was donated by Cytec and all other chemicals were purchased through Sigma Aldrich.

Table 1. Organic additives tested in the scoping study.

1	Citric acid
2	Cytec – Cyphos IL - 101 (IL - 101)
3	Guar
4	Humic acid
5	Malic acid
6	Polyacrylic acid (PAA) - 5200 MW
7	Polyethylene glycol (PEG) - 4000 MW and 8000 MW
8	Potato starch
9	Sodium acetate
10	Sodium dodecyl sulfate (SDS)
11	Sodium formate
12	Tetrabutylammonium chloride (TBAC)

4. Conclusions

Of the additives tested under Bayer predesilication conditions, both SEM and AccuSizer data have shown anionic surfactant SDS enhances individual DSP crystal growth when its concentration is between 250 to 750 mg/L. SDS within this concentration range was also shown to increase the proportion of agglomerates 8 - 40 μm in size and reduce the proportion of DSP fines ($< 1 \mu\text{m}$). In addition, a new intermediate phase with XRD peaks corresponding to zeolite 21 was formed when adding SDS, in contrast to the traditional DSP phase transformation pathway. However, the proportion of the zeolite 21 phase compared with zeolite A and sodalite phases was highly varied during the different concentrations and tests. The quaternary ammonium base TEAB also increased DSP crystal growth rate and reduced fines ($< 1 \mu\text{m}$) at 250 mg/L. The ionic liquid IL - 101 was shown to reduce the proportion of DSP fines ($< 1 \mu\text{m}$) at 100 mg/L. On the phase transformation DSP pathway, the results have shown humic acid, malic acid, PEG (8000 MW), SDS and TEAB enhance sodalite formation while CTAB conversely inhibits the conversion of zeolite A to sodalite.

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