MACROMOLECULAR ORGANIC BAYER PROCESS POISONS

by
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CERTIFICATE OF AUTHORSHIP

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person. This thesis does not contain material which to a substantial extent has been accepted for the award of any other degree or diploma of a university or other institute of higher learning, except where due acknowledgment is made in the text.

Damian Edward Smeulders.

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ABSTRACT

Sodium hydroxide is used at elevated temperatures to separate aluminium hydroxide from ferric oxide (red mud) in bauxite by the Bayer process. During the processing of the bauxite, the organic material that it contains is extracted into the Bayer liquor where it interferes with the precipitation of aluminium hydroxide. The organic material present in the Bayer process liquor from a high temperature alumina refinery operating at 250-255°C was examined in this study. Under these conditions large amounts of the acidified organic material was volatile (approximately 89% at 100°C, 0.1atm pressure under rotary evaporation). The non-volatile organic material obtained by rotary evaporation was fractionated by dialysis to produce different molecular weight fractions. These fractions have been analysed by thermal and spectroscopic methods (thermogravimetric analysis and calorimetry, nuclear magnetic resonance, infrared spectroscopy, pyrolysis gas chromatography mass spectrometry). It was discovered that the smallest molecular weight fraction (<1.2kD) appears to yield mainly hydroxybenzene carboxylic acids on pyrolysis and structurally resembles the highly oxidised humic acids that are found in the group of soils known as podsols. The 12-25kD and 25-50kD fractions appear to resemble material more akin to oxidised kerogen. The highest molecular weight material (>300kD) behaves as a soluble char.

Dialysis separates the organic material into molecular weight fractions, or more correctly fractions which can pass through specifically sized pores. As a result of the study of high temperature Bayer humic substances, it was discovered that the dialysis process appeared not to discriminate against certain small molecules. These small molecules, termed "guests", appear to be bound to larger macromolecules, "termed hosts", by physical entrapment. This may or may not also involve hydrogen bonding. Evidence for this supposition was obtained by proton nuclear magnetic resonance and by derivatisation of polar groups. Derivatisation released the entrapped small molecules which could then be detected and identified by gas chromatography mass spectrometry. It is suggested that host-guest humic complexes may also be prevalent in nature, where they have wide ramifications for the transport of organic matter in natural aqueous solutions such as streams, rivers and seas.

Prior to this study little was known about which molecular weight ranges of Bayer humic substances are particularly detrimental to the precipitation of aluminium hydroxide and sodium oxalate. The effects of the various molecular weight fractions (<1.2kD to >300kD) of organic matter introduced into alumina refineries with bauxite have been studied by precipitation testing. It was discovered that the effects produced by the organic materials were maximised under system stress, such as when there is competition for the number of sites at which new alumina carrying species or humic material can bind. The preparation of seed crystal is therefore very important and because of competition, effects are concentration dependent. Different molecular weight fractions of the humic substances were found to have different detrimental effects on precipitation yields of aluminium hydroxide and these did not correlate to changes in crystal surface area. While yields may be affected by ionic strength changes, it is clear that the higher molecular weight organics (>50kD), although present in low concentrations in Bayer process liquor, have particularly strong adverse affects on the dynamics of the precipitation of aluminium hydroxide. These larger molecular weight organics (>50kD) were also found to increase the stability of sodium oxalate in solution by about 20%. The impact of the organic fractions on the precipitation of aluminium hydroxide was found to be minimised through the use of caustic washed aluminium hydroxide seed.

In addition to the organic materials present in the Bayer process liquor, a number of insoluble organic materials are also produced from organic material entering the refinery with the bauxite. These insoluble organic materials appear in the waste solids termed "red mud", in the shell-side of the heat exchangers, on sodium oxalate crystals, on precipitated aluminium hydroxide "gibbsite", in precipitation tank scale, and on oxalate-gibbsite co-precipitation fines. These materials were analysed by pyrolysis gas chromatography mass spectrometry with in-situ methylation and by nuclear magnetic resonance spectroscopy to determine their compositions. Differences in composition can give information on the selectivity of the dissolution process and hence help in enhancing yields of alumina from the process. It was discovered that on pyrolysis each insoluble material produced different products. The pyrolysis products for the bauxite and red mud were found to differ considerably, with the red mud pyrolysates consisting mainly of aromatic polycyclics. However part of this difference was due to the red mud catalysing pyrolysis leading to the production of simple aromatic compounds. Nevertheless methanol soluble products were also found to be different in the red mud and bauxite.

The organic material recovered from the heat exchanger was found to be different to both the above materials, having characteristics similar to those of a light pitch or tar. The organic deposits in sodium oxalate and aluminium hydroxide crystals were also different, however they produced several common pyrolysis products including alkanes, alkenes, and long chain aliphatic carboxylic acids, predominantly with C_{14} to C_{16} carbon chain lengths, as well as short chain (C_4-C_7) aliphatic mono- and di-carboxylic acids. Not unexpectedly the organic material on the precipitation tank scale was similar in composition to soluble organic material in the process liquor.

As a result of this study we now have an understanding of the composition of both the soluble and insoluble organic materials present in a high temperature (250-255°C) Bayer alumina refinery. In addition we now know the molecular weight ranges of organic material responsible for many of the detrimental impacts on the operation of the Bayer process and we have a new concept in binding of humic materials, namely the "host-guest theory".