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MAX HT® BAYER SODALITE SCALE INHIBITOR: A GREEN SOLUTION TO ENERGY CONSUMPTION

Morris Lewellyn, Alan Rothenberg, Calvin Franz, Frank Ballentine, Frank Kula, Luis Soliz, Qi Dai, Scott Moffatt
Cytec Industries Inc., 1937 West Main Street, Stamford, CT 06904, USA

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Abstract

MAX HT® Bayer Sodalite Scale Inhibitor was developed to reduce or eliminate scaling from the evaporator and digester heaters in the Bayer process. This product has been successfully applied in 20 Bayer process plants worldwide, resulting in the significant benefits of increased heat transfer, reduced energy consumption and reduced acid waste from reduced heater cleanings. Based on trial data from a number of plants, the estimated annual savings per ton of alumina produced are 0.26-1.3 Gj energy, resulting in 13-92 kg reduction in CO_2 emissions, and 0.9-2.7 kg reduction in acid waste. When these savings are applied to the total alumina production from the 20 plants, this leads to an estimated realized annual savings of 11-56 million Gj energy, 0.54-3.9 billion kg CO_2 emissions, and 38-116 million kg of acid waste reduction. For this reason, MAX HT was awarded the 2012 EPA Presidential Green Chemistry Challenge Award.

Introduction

Cytec has developed a line of polymers for use as scale inhibitors in evaporator and digester heaters used in the Bayer process [1-8]. These products provide benefits by reducing or eliminating the scale formation in the heaters resulting in significantly higher heat transfer, reducing energy consumption and waste. These products have been successfully applied in a number of plants utilizing the Bayer process throughout the world [9-11]. This technology is also being assessed for sodalite scale elimination in the evaporation process for the treatment of other types of substrate [12].

The scale deposited in these heaters is sodium aluminosilicate – sodalite or DSP (desilication product). This is a result of the silica that is present in bauxite ores as silicates, primarily clay minerals, that dissolves quickly under typical Bayer alumina digestion conditions. The Bayer liquor remains supersaturated in silica and this supersaturation is greatest after the alumina precipitation step, i.e. in the spent liquor. As the alumina-depleted liquor is reheated, the rate of silica precipitation in the form of sodalite increases markedly with increasing temperature due to faster kinetics [13]. This precipitation occurs as scaling on the inside of the heat exchange tubes and a significant loss of heat transfer occurs, leading to increased energy consumption, increased caustic losses, reduced liquor flows, reduced throughput, reduced evaporation, and reduced production.

Without MAX HT, the method used to manage the sodalite scale problem is to clean out the system whenever the heat exchanger performance drops below a certain level, typically about half the original heat transfer rate. This cleaning is generally accomplished with the use of a 5-10% sulfuric acid solution to dissolve the scale. The used acid constitutes a waste stream requiring disposal. In addition to the acid cleaning, much of the inter-stage piping is cleaned using mechanical means, such as jackhammers, to remove the scale.

The use of MAX HT is one way to make the Bayer process greener in terms of energy use and waste generation. MAX HT is commercial at twenty different plants across the globe, and under evaluation at a number of other plants. Many of these are double stream plants where the scale inhibitor can be used on both evaporator and digester heaters, but there are a number of single stream plants that find benefits from just treating the evaporator heaters. This paper will explore some of the data on energy savings generated in plant trials to estimate the range of energy savings that can be realized. This estimate of the potential energy and waste savings is the basis for the awarding Cytec the 2012 U.S. EPA (Environmental Protection Agency) Presidential Green Chemistry Challenge Award for MAX HT.

Development of the MAX HT Technology

Several possible approaches to solving the sodalite scale problem were considered by our research team and others. These included 1) seeding the liquor to precipitate sodalite, 2) modification of the sodalite crystal morphology with the hope that it would be less adherent, 3) coating the surfaces to reduce sticking, and 4) developing a reagent to inhibit the growth of the sodalite crystal. The first three approaches were found unsuitable either because of the cost associated with the approach or that it did not work very well.

A group of scientists dedicated to this project worked to develop a correlation of inhibitor activity with structure. It was discovered that the functional group necessary for inhibitor activity was the silane group: $-Si(OR)_3$ where R can be H, C_1-C_3 alkyl, or Na. For optimum performance, this functional group was attached to a polymer. This means that a wide variety of materials are possible for the polymeric backbone and other substituents may also be incorporated [1-4]. Therefore, the MAX HT technology encompasses a broad family of polymers. The polymers used in this technology can be made in a variety of ways, and a generic structure is shown in Figure 1.

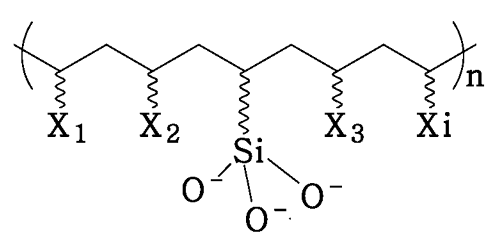

Figure 1. Generic structure for MAX HT antiscalants.

The scale inhibition mechanism occurs as the silane group interacts with the growing aluminosilicate crystal either by incorporation into the crystal or by adsorption onto the growing crystal surface in such a way that the crystal growth is stopped. The mechanism is depicted schematically in Figure 2 and is based on the classical mechanism for crystallization and inhibition where the overall free energy goes through a maximum at the critical size of the micronuclei [14]. This means that if the growth is stopped before the micronuclei reach the critical size, the driving force for the crystal is to go back into solution which is at a lower energy level. This explains why MAX HT is so effective at a low dose, which is well below what would be a stoichiometric dose if the mechanism was a simple chelation of silica in solution.

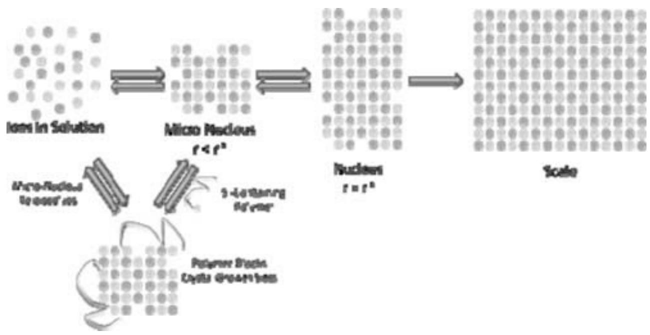

Figure 2. MAX HT interacts with micronuclei preventing growth to nuclei.

Plant Experience

Benefits from using MAX HT previously reported [3-6] are summarized in Figures 3-5. Scaled heater tubes and declining heat transfer are changed into clean tubes and constant heat transfer when MAX HT was used.

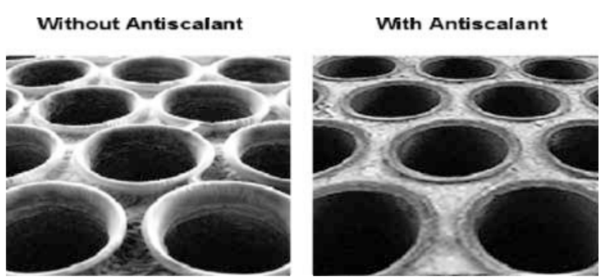

Figure 3. Dirty and clean heat exchangers from operating without and with MAX HT antiscalant after 160 hrs. of continuous operation, corresponding to the heat transfer curves in Figs. 4 and 5, respectively.

Sodalite scale inhibitor MAX HT is used commercially to eliminate and/or minimize scaling in evaporator and digestion heater tubes at dosages ranging from 20-40 ppm. Without the use of MAX HT, plants have minimal control on the rate of scaling in these heater tubes. Heater cleaning cycles vary from about 5 days to 60 days depending on chemistry of the liquor, amount of silica in the particular bauxite ore, de-silication, operating temperature in heaters, etc. Current practice is to acid wash or mechanically clean heater tubes on a regular cycle to maximize benefits realized from operating with clean heaters. MAX HT has allowed plants to gain control or completely eliminate the formation of sodalite scale in heaters and interstage piping.

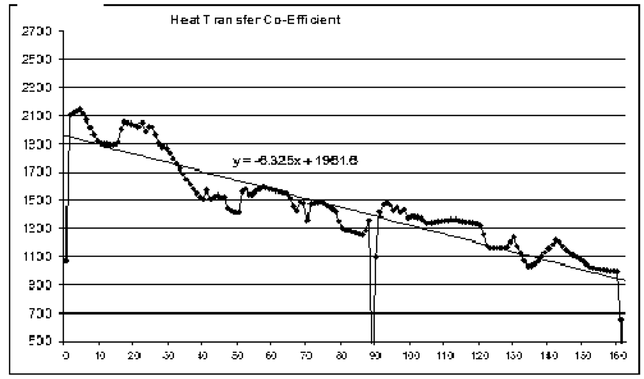

Figure 4. Typical heat transfer decay during 160 hrs. without MAX HT. X-axis is in hours.

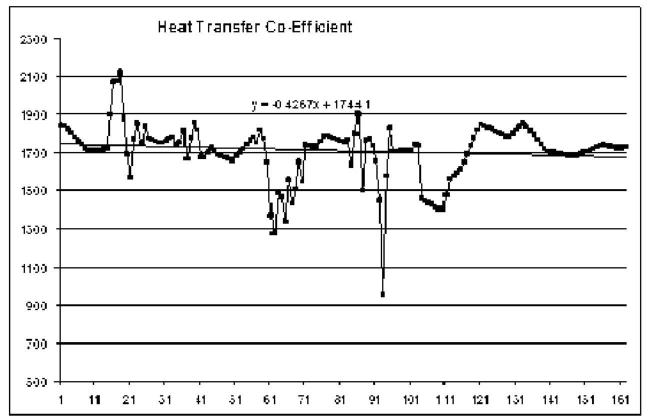

Figure 5. Constant heat transfer coefficient resulting from the use of MAX HT. X-axis is in hours.

Benefits of MAX HT

MAX HT sodalite scale inhibitor has been used successfully in a number of Bayer process plants [6-11]. Typically, the on-stream time for a heater is increased from some 8-10 days to 45-60 days for digestion and 20-30 days to >150 days for evaporators. This ability to maintain a high heat transfer over a much longer life cycle between cleanings has resulted in a number of benefits. These benefits are summarized below.

1. Increased evaporation when used in the evaporator heaters. This leads to reduced caustic consumption and improved mud washing in the washer circuit because more water is available for efficient washing of the red mud and gibbsite crystals. The annual realized reduction of caustic is estimated to be 79,000-198,000 tons of 50% caustic.
2. Increased production. This is a result of an increased average flow due to being able to maintain the outlet temperature without having to reduce flow to accommodate a lower heat transfer rate.
3. Reduced energy consumption realized per annum. Savings in the range of 4.4-22.0 million tons of steam have been realized, which translates to 11-56 million Gj energy, or 0.54-3.9 billion kg CO_2.

4. Less direct steam to the digester when used in the digester heaters. By being able to maintain the maximum live steam heater outlet temperature, the need to add steam by direct injection in the digesters is reduced or eliminated, resulting in less extraneous dilution which impacts soda recovery and therefore caustic consumption. This also allows more mass in the digester in terms of liquor and bauxite leading to higher production.
5. Reduced digester and evaporator heaters cleaning and maintenance. This leads to a reduction in cost for the acid, labor, tube changes, etc. There is also less exposure of the workers to the associated hazards. The realized annual reduction in hazardous acid waste is 38-116 million kg. The number of cleaning cycles can be reduced from a range of 20-50 per year per heater train to less than 10 per heater train.
6. Steadier plant operation.

The results obtained from several plant trials of 7 days or longer detailed below will illustrate the benefits that are obtained from using MAX HT. The criteria and results measured varied from plant to plant, but all have shown improved heater operation.

Plant 1 is a high temperature digestion plant in which the MAX HT was dosed to the digester heaters at 35 ppm. The results are shown in Table I.

Table I. Trial Results from Plant 1

Measured Criteria	Without MAX HT	With MAX HT
Production, tons alumina per day	4613	4681
Total steam, t/t alumina	3.27	3.15
Last indirect heater temperature, ºC	209.3	211.9
Live steam heater temperature, ºC	224.2	228.0

The use of MAX HT in the digester heater train allowed for higher heat transfer due to reduced scaling resulting in higher production (they were able to push more through the heaters), reduced steam production per ton of alumina produced (greater efficiency from the recovered steam from the process), and higher temperature for digestion resulting in greater efficiency in the digester.

Plant 2 is a high temperature digestion plant where the MAX HT was dosed to the digester heater train at about 30 ppm. The results from this trial are shown in Table II.

Table II. Trial Results from Plant 2

Measured Criteria	Without MAX HT	With MAX HT
Liquor flow, m^3/hr	890	951
Live steam heater exit temperature, ºC	204.8	211.9
Heat transfer to liquor (Gj/hr)	498	563

Again, there is a significant increase in heat transfer for Plant 2, resulting in increased liquor flow, higher exit temperature, and higher overall heat transfer to the liquor.

Plant 3 is a plant where the MAX HT was dosed only to the evaporator at a dose of about 35 ppm. The results are shown in Table III.

Table III. Trial Results from Plant 3

Measured Criteria	Without MAX HT	With MAX HT
Flow, m^3/hr	1085	1180
Evaporation, t H_2O/hr	169	197
Steam, t/hr	46.9	43.2
Evaporation Economy, t H_2O/t steam	3.6	4.8

By using MAX HT, the increased efficiency for the heat transfer from the recovered heat in the earlier heaters in the evaporator train resulted in higher evaporation with less generated steam. They were also able to increase the flow through the evaporator while obtaining the higher evaporation rate.

Plant 4 is a plant where the MAX HT was dosed to the evaporator at a dose of 35 ppm. The results from this trial are shown in Table IV.

Table IV. Trial Results from Plant 4

Measured Criteria	Without MAX HT	With MAX HT
Steam flow, t/hr	21.7	22.5
Liquor flow, m^3/hr	507	553

Although the steam flow went up slightly, the liquor flow increased significantly, resulting in a lower steam usage per unit of production in this plant.

Plant 5 is another plant where the MAX HT was dosed to the evaporator feed at a dose of about 35 ppm. The results from this trial are shown in Table V.

Table V. Trial Results from Plant 5

Measured Criteria	Without MAX HT	With MAX HT
Feed rate, t/hr	447.9	543.5
Steam flow, t/hr	17.3	18.9
Live steam temperature, ºC	155.4	153.8
Evaporation, t H_2O/hr	74.0	81.1

The increased heat transfer in the earlier heaters in the train which use recovered heat from the plant has resulted in a significant increase in flow and evaporation. The live steam temperature was lower with MAX HT which reflects their ability to transfer heat; therefore, they can use a lower steam temperature (lower steam pressure) to obtain the evaporation that they needed.

Value of the MAX HT Technology

The value of the MAX HT technology is to reduce energy usage by 0.26-1.3 Gj, reduce CO_2 emissions by 13-92 kg, and reduce waste generation by 0.9-2.7 kg per ton of alumina produced. There are about 73 operating Bayer plants throughout the world, ranging in production capacity of 0.2 to 6 million tons of alumina annually, with the majority being in the 1.5 to 3 million tons capacity. The estimated annual environmental benefit for the 20 commercialized plants is shown in Table VI along with the estimated global annual potential benefit based on 2011 figures.

Table VI. Potential and Realized Benefits of MAX HT Technology

	Energy (Gj)	**CO_2 Reduction (Kg)**	**Waste Reduction (Kg)**
Savings per ton of alumina produced	0.26-1.3	13-92	0.9-2.7
Realized savings (20 commercial plants)	11-56 million	0.54-3.9 billion	38-116 million
Potential savings (All 73 plants)	25-128 million	1.3-8.9 billion	86-263 million

Conclusions

1. MAX HT provides estimated annual savings per ton of alumina produced of 0.26-1.3 Gj energy, resulting in 13-92 kg reduction in CO_2 emissions and 0.9-2.7 kg reduction in acid waste.
2. This more efficient use of energy results in increased evaporation in the evaporator heaters, leading to reduced caustic consumption and more efficient use of water.
3. The use of MAX HT leads to increased production due to an increase in average flow and reduced direct steam injection.
4. The use of MAX HT also results in reduced cleaning of digester and evaporator heaters resulting in reduced exposure of workers to the hazards and reduced acid waste.

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