Cytec Industries Inc. 2012 Green Chemistry Challenge Award Nomination

Sodalite Scale Inhibitor

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MAX HT™ Bayer Sodalite Scale Inhibitor

Milestones in Last 5 Years

The first commercial full plant operation using MAX HT™ Bayer Sodalite Scale Inhibitor occurred in 2004. Patents have issued on this technology in more than 17 countries in the last 5 years and include: US 7,390,415 (June, 2008), US 7,442,755 (October, 2008), and US 7,674,385 (March, 2010). At present, this product is commercial in 18 plants and in various stages of trialing in another 7 plants throughout the world. A second generation product was commercialized in 2007 which has higher tolerance to un-dissolved solids in the circuit.

Focus Areas: The Use of Greener Reaction Conditions and **Design of Greener Chemicals**

This technology fits into the focus areas of the use of greener reaction conditions and the design of greener chemicals because these products enable a novel process method that reduces pollution at its source and reduces energy in use. This technology prevents the formation of sodalite scale in heat exchangers used in the Bayer process of bauxite ore to produce alumina, thus requiring less equipment clean-outs and generating less waste. In addition, this improves heat transfer rates, thus minimizing energy expended in the process. This leads to more efficient use of energy and a reduction in waste at its source. This does not meet the criteria for a small business or academia.

Collaboration

The MAX HT technology was developed solely in the United States in the Cytec Technology Center in Stamford, CT.

Abstract

The Bayer process converts bauxite ore to alumina, the primary raw material for aluminum. The heat exchangers and inter-stage piping in the process build up sodalite scale (i.e., aluminosilicate crystals), which reduces the efficiency of the heat exchangers. The equipment must be taken off line periodically and cleaned with sulfuric acid.

Cytec developed its MAX HT™ Bayer Sodalite Scale Inhibitor products for the Bayer process. There are no other scale inhibitors on the market for this application. The active polymeric ingredient contains silane functional groups that inhibit crystal growth by incorporation into the crystal or adsorption onto its surface. Dosages range from 20 to 40 ppm. Assessments of these polymers under EPA's Sustainable Futures Program indicated low overall concern for human health and the aquatic environment.

Eliminating sodalite scale from heater surfaces produces many benefits. Heat recovery from the steam produced in various unit operations is more efficient. Increased evaporation makes the countercurrent washing circuit more efficient and reduces caustic losses. Reducing the use of steam reduces emissions from burning carbon-based fuels. Lastly, reducing the sulfuric acid used to clean heaters reduces both worker exposure and waste.

There are about 73 operating Bayer process plants worldwide with annual capacities of 0.2–6 million tons of alumina; most plants are in the 1.5–3 million ton range. Eighteen Bayer process plants worldwide have adopted this technology; 7 more plants are testing it. Each plant using MAX HT™ saves $2–20 million annually. The realized annual energy savings are 9.5-47.5

trillion BTU which is the equivalent of about 1.1-7.7 billion pounds of carbon dioxide not released to the atmosphere. Fewer cleaning cycles and less acid per cycle result in a realized annual hazardous waste reduction of 76-230 million pounds.

Introduction

Cytec has developed a line of polymers for use as scale inhibitors in evaporator and digester heaters used in the Bayer process [1-6]. 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 [7-8]. There are no other anti-scalants on the market for this application. This technology is also being assessed for sodalite scale elimination in the evaporation process for the treatment of other types of waste [9].

The Bayer process is a technology whereby alumina trihydrate is extracted from bauxite ore using hot caustic solution. After separating the insoluble solids from the pregnant liquor, the alumina trihydrate is precipitated from the liquor and the spent liquor is recycled. Heat exchangers are used in the evaporation and digestion circuits to re-concentrate the liquor to the optimum caustic concentration and then to heat the liquor to the proper temperature for digestion. Silica that is present as silicates, primarily clay minerals, dissolves quickly under typical Bayer alumina digestion conditions, resulting in liquor that is supersaturated in silica, particularly after precipitation. The silica in the liquor reacts with the caustic and alumina on the hot surfaces of the heat exchangers to form sodalite which coats the inner surfaces, leading to poor heat transfer.

The current method used in the Bayer industry to manage the sodalite scale problem is to clean out the system whenever the heat exchanger performance drops below a certain level. There is no anti-scalant available on the market today. In the acid cleaning process, sulfuric acid is used at a concentration of 5-10% to dissolve the sodalite 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.

While the Bayer process may not be considered a totally green process per se, the use of MAX HT is a way to make the process greener in terms of energy use and waste generation with the use of safe materials. The Pre-Manufacture Notification for the polymeric substances in MAX HT was assessed and submitted to the EPA under the Sustainable Futures Program (PMN numbers P04-800, P08-191, P08-192, and P08-193). The Sustainable Futures assessments on all polymers shown below and in our PMN submissions indicate a "Low Overall Concern" for human health and the aquatic environment. Further testing on one of the polymers cleared under a PMN has confirmed that it is low in acute toxicity (acute oral (rat) LD50 >5,000 mg/kg) and not classified as dangerous for the environment (the 72 hour EC50 in green algae is 150 mg/l, the 48 hour daphnia EC50 is 770 mg/l, and the 96 hour fish LC50 is >100 mg/l).

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. It was also determined that this functional group needed to be attached to a polymer rather than as a monomer or small molecule for optimum performance. This means that a wide variety of materials are possible for the polymeric backbone and other substituents may also be incorporated. Therefore, the MAX HT technology encompasses a broad family of polymers.

The polymers used in the MAX HT technology contain proprietary structures with molecular weights in the range of 10,000-30,000. The polymers used in this technology can be made in a variety of ways. They can be made by polymerizing a monomer containing the silane group or by a reaction of a polymer backbone with a reagent containing the silane group (see Figures 1 and 2).

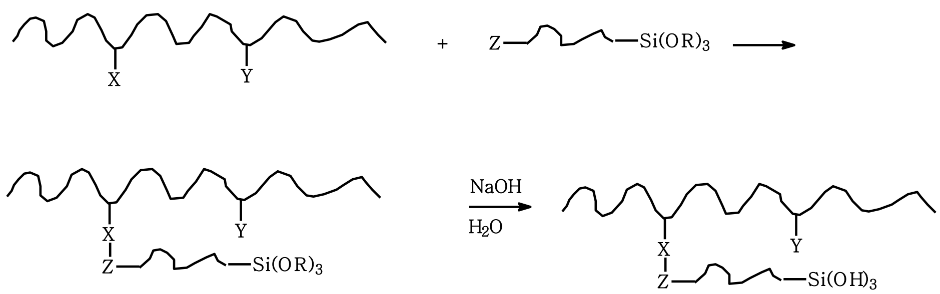

Figure 1. Generic post-polymerization modification process for MAX HT

Table 1. Examples of polymers made by post-polymerization modification

1:1 Styrene-maleic anhydride copolymer (~16,000 MW) reacted with 8 mole% (3-aminopropyl)triethoxylsilane and 50 mole% butylamine (mole% based on maleic anhydride units)
Polyethyleneimine (~25,000 MW) reacted with 3 mole% (3-chloropropyl)trimethoxysilane
Polyethylene oxide (~2000 MW) reacted with 2.2 mole% 3-glycidoxypropyltrimethoxysilane
Polyethyleneimine (~2000 MW) reacted with 4 mole% 3-glycidoxypropyltrimethoxysilane and 5 mole% glycidyl 4-nonylphenyl ether

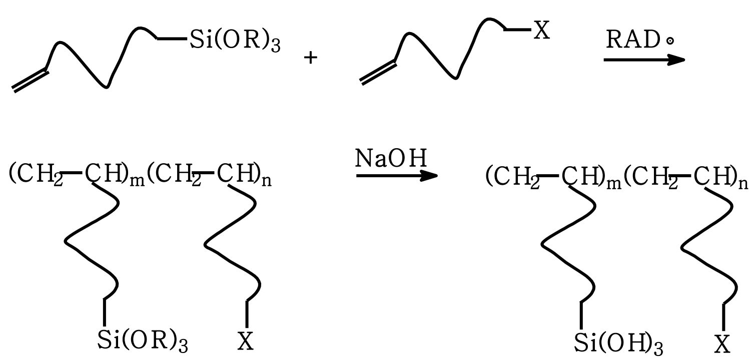

Figure 2. Generic free radical polymerization of silane containing monomer

Table 2. Examples of polymers made by free radical polymerization of silane monomer

Silane Monomer	Other Monomers
8.5 mole% vinyltriethoxysilane	21.5 mole% acrylamide, 70 mole% acrylic acid
5 mole% N-(3-triethoxysilyl)propylacrylamide	95 mole% 1-vinyl-2-pyrrolidinone

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 3 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. 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. Full chemical composition/structures are confidential business information, but have been submitted to the EPA under PMN numbers P04-800, P08-191, P08-192, and P08-193.

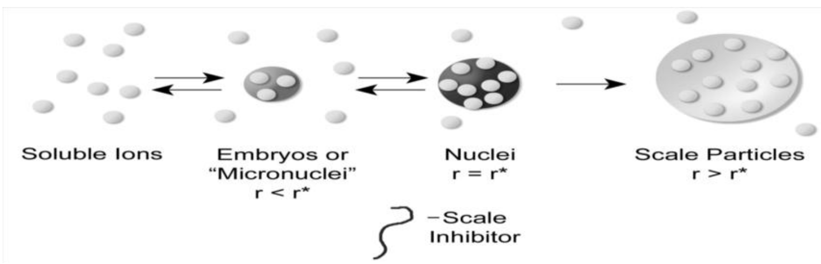

Figure 3. MAX HT interacts with micronuclei preventing growth to nuclei

Plant Experience

Benefits from using MAX HT previously reported [3-6] are summarized in Figs. 4-6. Scaled heater tubes and declining heat transfer are changed into clean tubes and constant heat transfer when MAX HT was used.

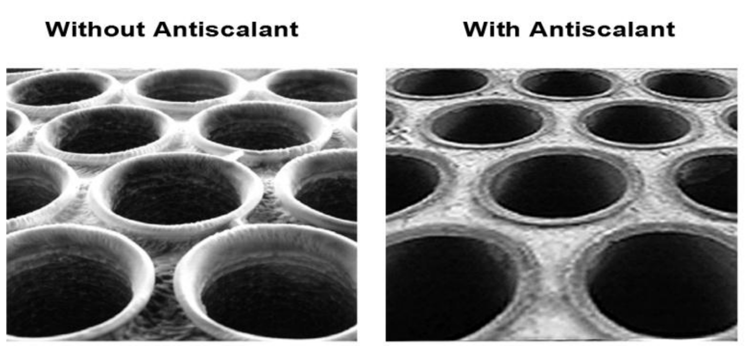

Figure 4. Dirty and clean heat exchangers from operating without and with MAX HT anti-scalant after 160 of continuous operation, corresponding to the heat transfer curves in Figs. 5 and 6, respectively.

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.

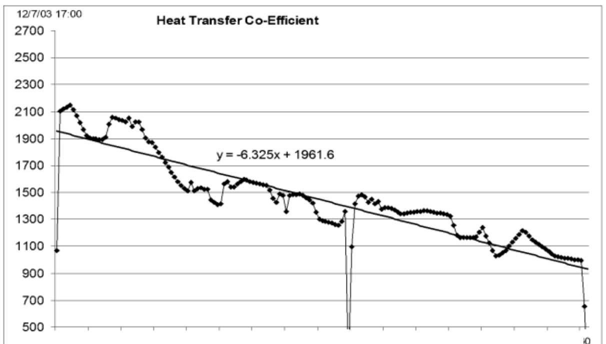

Figure 5. Typical heat transfer decay during 160 hours without MAX HT. X-axis is in hours.

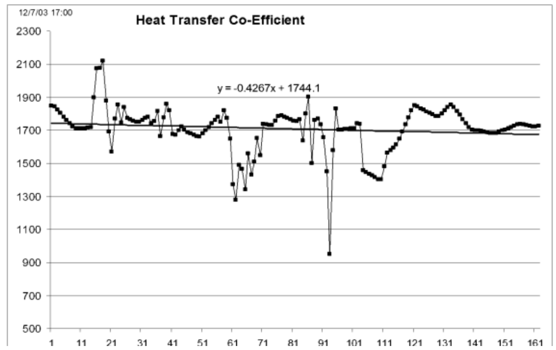

Figure 6. Constant heat transfer coefficient resulting from the use of MAX HT. X-axis is in hours.

Benefits of MAX HT

MAX HT sodalite scale inhibitor has been used successfully in a number of Bayer process plants [4-8]. 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 settling 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 4.0-19.8 million tons of steam have been realized, which translates to 9.5-47.5 trillion BTU, or 1.1-7.7 billion lbs 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.
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 76-230 million pounds**. 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 two 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 3.

Table 3. 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 4.

Table 4. 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.

Value of the MAX HT technology

The value of the MAX HT technology is to **reduce energy usage** by 0.25-1.25 million BTU, **reduce CO2 emissions** by 29-202 lbs, and **reduce waste generation** by 2-6 lbs per ton of alumina produced. Generally, the **cost savings** to the plant will be in the range of $2-$6 per ton of alumina produced. This represents a 1-3% savings in the manufacturing cost of alumina. 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 18 commercialized plants is shown in the table below along with the estimated global annual potential benefit based on 2011 figures.

Potential and Realized Benefits of Max HT Technology				
	BTU energy	**CO2 reduction**	**waste reduction**	**US dollars saved**
Savings per ton of alumina produced	0.25-1.25 million	29-202 lbs	2-6 lbs	$2-6
realized savings	9.5-47.5 trillion	1.1-7.7 billion lbs	76-230 million lbs	$76-230 million
potential savings	24-121 trillion	2.8-19.6 billion	190-580 million lbs	$190-480 million

Currently, this technology is commercial in 18 plants and is in various stages of evaluation at another 7 plants. In the United States, there are a total of 3 Bayer plants operating throughout the year, with two plants using MAX HT commercially and the third one evaluating it. In addition, a fourth U.S. plant has just recently come back on line after being shut down for a few years. It is anticipated that this plant will resume using MAX HT early in 2012.

References

1. D. Spitzer, A. Rothenberg, H. Heitner, and F. Kula, "Method of preventing or reducing aluminosilicate scale in a Bayer process," U.S. patent 6,814,873B2 (2004).
2. H. Hetiner and D. Spitzer, "Hydrophobically modified polyamine scale inhibitors", WO patent 2008045677 (2008).
3. D. Spitzer, A. Rothenberg, H. Heitner, F. Kula, M. Lewellyn, O. Chamberlain, Q. Dai, and C. Franz, "Reagents for the elimination of sodalite scaling", Light Metals, 183-188 (2005).
4. D. Spitzer, A. Rothenberg, H. Heitner, F. Kula, M. Lewellyn, O. Chamberlain, Q. Dai, and C. Franz, "A real solution to sodalite scaling problems," Proceedings of the 7th International Alumina Quality Workshop, 153-157 (2005)
5. D. Spitzer, O. Chamberlain, C. Franz, M. Lewellyn, and Q. Dai, "MAX HT Sodalite Scale Inhibitor: Plant experience and impact on the process", Light Metals, 57-62 (2008).
6. M. Lewellyn, A. Patel, D. Spitzer, C. Franz, F. Ballentine, Q. Dai, O. Chamberlain, F. Kula, and H. Chen, "MAX HT Sodalite Scale Inhibitor: Plant experience with first and second generation products," Proceedings of the 8th International Alumina Quality Workshop, 121-124 (2008).
7. A. Oliveira, J. Dutra, J. Batista, J. Lima, R. Diniz, R, and E. Repetto, "Performance appraisal of evaporation system with scale inhibitor application in Alunorte plant", Light Metals, 133-136 (2008).
8. L. Riffaud, P. James, E. Allen, and J. Murray, "Evaluation of sodalite scaling inhibitor – A user's perspective", International Symposium on Aluminum: From Raw Materials to Applications – Combining Light Metals 2006 and the 17th International ICSOBA Symposium, Montreal, Quebec, Canada, October 1-4, 2006. Bauxite & Alumina session, paper 29.7.
9. L. N. Oji, T. L. Fellinger, D. T. Hobbs, N. P. Badheka, W. R. Wilmarth, M. Taylor, E. A. Kamenetsky, and M. Islam, "Studies of potential inhibitors of sodium aluminosilicate scales in high-level waste evaporation", Separation Science and Technology, 43, 2917-2928 (2008).