Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Studies of Potential Inhibitors of Sodium Aluminosilicate Scales in High-Level Waste Evaporation

L. N. Oji[a]; T. L. Fellinger[a]; D. T. Hobbs[a]; N. P. Badheka[a]; W. R. Wilmarth[a]; M. Taylor[b]; E. A. Kamenetsky[b]; M. Islam[b]
[a] Savannah River National Laboratory, Aiken, SC, USA [b] Cytec Industries, Inc., Stamford, CT, USA

To cite this Article Oji, L. N. , Fellinger, T. L. , Hobbs, D. T. , Badheka, N. P. , Wilmarth, W. R. , Taylor, M. , Kamenetsky, E. A. and Islam, M.(2008) 'Studies of Potential Inhibitors of Sodium Aluminosilicate Scales in High-Level Waste Evaporation', Separation Science and Technology, 43: 9, 2917 — 2928
To link to this Article: DOI: 10.1080/01496390802121958
URL: http://dx.doi.org/10.1080/01496390802121958

Separation Science and Technology, 43: 2917–2928, 2008

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802121958

Taylor & Francis
Taylor & Francis Group

Studies of Potential Inhibitors of Sodium Aluminosilicate Scales in High-Level Waste Evaporation

L. N. Oji,[1] T. L. Fellinger,[1] D. T. Hobbs,[1] N. P. Badheka,[1] W. R. Wilmarth,[1] M. Taylor,[2] E. A. Kamenetsky,[2] and M. Islam[2]
[1]Savannah River National Laboratory, Aiken, SC, USA
[2]Cytec Industries, Inc., Stamford, CT, USA

Abstract: For a decade, the evaporation of highly alkaline High-Level nuclear wastes as practiced in some DOE nuclear waste facilities has produced sodium aluminosilicate scales causing both operation and criticality hazards. Segregation of aluminum-rich wastes from silicate-rich wastes minimizes the amount of scale produced and reduces cleaning expenses but does not eliminate scaling nor increase operational flexibility in waste processing. Similar issues have affected the aluminum refining industry for many decades. Over the past several years, successful commercial products have been identified to eliminate aluminosilicate fouling in the aluminum industry but have not been utilized in a nuclear environment.

Laboratory quantities of three proprietary aluminosilicate scale inhibitors produced by Cytec industries have been shown to prevent formation of aluminosilicate scales. The Savannah River National Laboratory (SRNL) has been actively testing these potential scale inhibitors to examine their radiation stability, radiolytic degradation behaviors, and downstream impacts to determine their viability within the High-Level nuclear waste system at the Savannah River Site (SRS). One of the tested polymers has been found to successfully meet the established criteria for application in the nuclear waste environment.

Keywords: Antiscalant, cancrinite, nuclear waste evaporator, scale inhibitor, sodalite, sodium aluminosilicate

Received 20 October 2007; accepted 10 April 2008.
Address correspondence to L. N. Oji, Savannah River National Laboratory, P. O. Box X, 29808 Aiken, SC, USA. E-mail: lawrence.oji@srnl.doe.gov

INTRODUCTION

Effective mitigation of scale formation in process plants is a serious issue of major scientific and technological challenge to the minerals, chemicals, petrochemical, power generation, and food processing industries worldwide. Many industrial operations involve intensive heating and cooling duties performed in heat exchangers where fouling tends to be most profound. Fouling management or mitigation methods usually require enormous human effort with plant personnel manually de-scaling equipment off-line and often using highly corrosive, acidic/caustic reagents and/or power tools. Sodium aluminosilicate (NAS) scale deposition occurs in heat exchangers and other vessels of caustic media processing industries comprising Bayer process alumina refineries (1–4), Kraft pulp and paper closed cycle mills (5–7), and the evaporation of highly alkaline nuclear wastes (8,9). Fouling can be so severe that complete blockage of alumina plant tubular heat exchangers may sometimes occur within 4–6 weeks of operation. When NAS fouling occurs in nuclear waste processing, dissolved radionuclides (e.g. uranium-235, plutonium-238 and cesium-137) may also exceed their solubility limits. This eventually causes mixed NAS – radionuclide precipitation and fouling introducing criticality issues for cleaning operations (10–12).

The development of potential NAS inhibitors has been studied for many decades. Addai-Mensah, et al. (13) describes use of an unidentified polymeric additive that reduced sodalite scaling on steel surfaces by $\sim$37% at a loading of 300 mg/L. Fouling of the SRS nuclear waste evaporator from NAS scale deposition has had a significant impact on nuclear waste evaporation and processing at SRS. The mitigation or minimization of fouling has led to feed segregation and reduced waste processing flexibility. Additionally, cleaning costs in the nuclear environment have proven to be substantial. Application of a scale inhibitor, therefore, has advantages. However, a successful deployment must meet the following attributes:

- Delays the formation of NAS in the evaporator
- Has a short life span under radiation fields to precipitate NAS in the drop tanks of the evaporator systems
- Does not generate flammable gases upon decomposition (radiolytic/chemical) of the polymeric additive, and
- Does not have any downstream impacts

Personnel from Cytec Industries (14) showed that a patented product could eliminate scaling in the Bayer industry and have been successfully introducing this product worldwide. As a result of contact between Cytec

and Savannah River Site representatives, three NAS inhibitor candidate test samples have been examined for application in the High Level Waste evaporators at SRS.

EXPERIMENTAL

Cytec Industries, Inc. provided three proprietary inhibitors for testing. In this manuscript, these three antiscalant polymers are designated as Epsilon, Omega, and Tau. The three prospective agents were evaluated to determine their laboratory scale performance capabilities in the suppression of NAS formation. In this study, the effectiveness of these inhibitors at preventing the formation of NAS solids from simulated waste liquors containing high levels of aluminum (0.3 M) and silicon (0.025 M) as a function of radiation dose were examined. The base liquor in these tests were a solution containing 6 M sodium with 4 M total free-hydroxide ion, 1 M nitrate and 1 M nitrite ions. The performance of these three antiscalant at suppressing NAS formation in an actual nuclear waste supernatant was also examined.

In this study, the radiation stability of the proposed NAS inhibitors was examined. Two forms of testing were conducted. First, tests were performed where the inhibitor agents were placed in a waste simulant that contained aluminate ion and irradiated to a specific radiation dose. In these tests, the inhibitor agents were added at the expected performance level (300 ppm). After irradiation, the silicon ion in the form of sodium silicate was added and the mixture heated for 24 hours at 100°C. In the second set of tests, the inhibitors were added at a higher concentration (1500 ppm), irradiated to a specific radiation dose and then analyzed by size exclusion chromatography.

Most of these tests involved irradiating 100 mL portions of simulant solutions containing low concentrations of each inhibitor to a prescribed gamma dose. Simulants were irradiated in 150-mL capacity stainless steel tubes. After irradiation, the stainless steel tubes were placed in an oven for 24 hours at 100°C. At the end of the oven treatment, the resulting solution was processed through a 0.45 μm filter and the filtrate submitted for Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES) analysis for silicon and aluminum content. The resulting solid fraction was dried at 100°C for 40 minutes and weighed.

Control tests that did not include antiscalants in the simulant were also treated as described above and used as reference material. These resulting solid fractions (NAS) from these reference tests were performed for the purpose of comparison to determine the extent of NAS suppression or growth based on the reference data.

To calculate the relative percent scale growth, the average amount of dried solid fraction, if any, from samples containing each inhibitor was divided by the average amount of dried solid fraction from the reference samples and multiplied by 100 to get the value for normalized scale growth (%) relative to the reference runs which did not contain inhibitor.

An "actual" waste test, one designed to examine the effectiveness of the inhibitors in the presence of nuclear waste obtained directly from an SRS nuclear waste tanks, was also performed. The tests examined control tests without antiscalant polymers versus ones in which the antiscalant polymer was added. The radioactive waste sample used for this section of the tests was a composite nuclear waste supernatant sample which was used in a previous study (15). For this test, adjustments for free-OH, silicon and boron levels were made to bring their concentration levels, respectively, to 4.0 molar, 687.5 mg/L, and 221.6 mg/L. To adjust these species the following precursors were used per 500-mL volume capacity: sodium hydroxide (81.63 g pellets), sodium silicate-solution D (2.36 g-PQ Corporation) and sodium borax (1.041 g). This level of boron ensured that the silicon to boron ratio was 3 : 1, which is assumed to be typical of SRS nuclear waste stream in general. The final adjusted levels for free-OH and silicon were analytically determined to be, respectively, 5.30 molar and 758 mg/L. The density of the resulting adjusted composite solution was 1.25 g/mL.

In the actual waste tests, each inhibitor agent, at 300 ppm levels, was mixed thoroughly with 125 g of the adjusted composite nuclear waste in different 250-mL capacity poly-bottles before introduction of the mixture into a reflux reaction vessel. After heating (100°C) and refluxing for 16 hours, the resulting liquor was processed as described above. The resulting solids, if any, were washed several times with de-ionized water and vacuum dried for 72 hours before determination of weights of solids left on the filter membranes, if any. The reference test was also performed in duplicate with a composite sample which did not contain any of the antiscalant polymers.

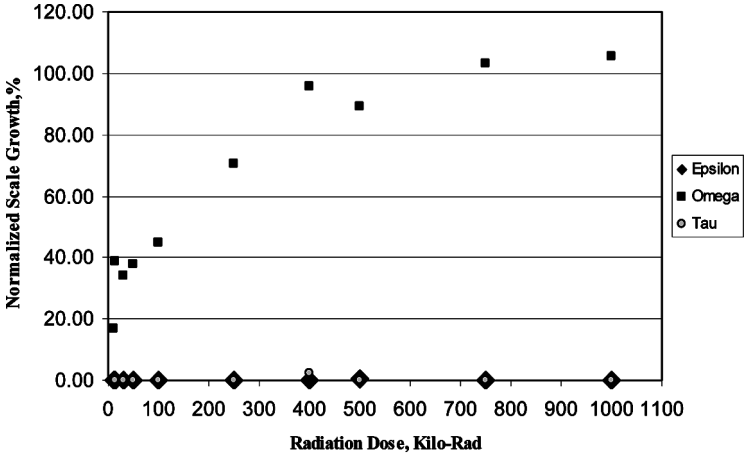
Radiation tests were performed using two types of dry Cobalt-60 gamma sources (J. L. Shepherd Model 109-chamber size is 6" × 8" and variable dose irradiation-J. L. Shepherd Model 484) capable of irradiating a variety of solid and liquid materials at dose rates ranging from 1 R/Hr to 2.0 E 6 R/Hr. The J. L. Shepherd Model 484 Chamber size is 10" × 10" × 40" allowing for larger samples to be irradiated.

RESULTS AND DISCUSSSION

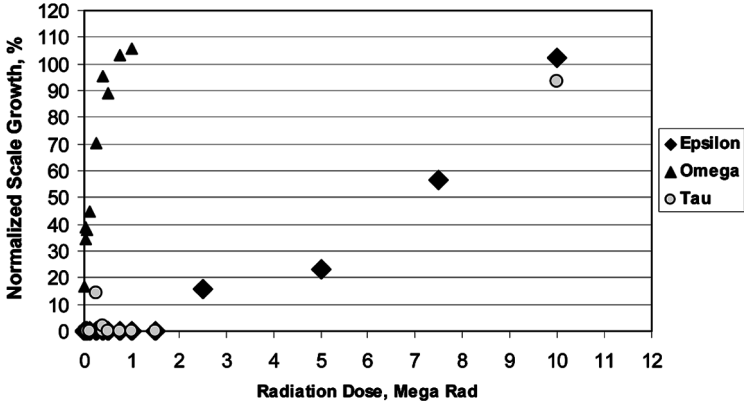
To determine the extent of NAS suppression during the hydrothermal synthesis of NAS, changes in the amount of NAS formed relative to

the reference runs without the antiscalant and initial/final silicon concentrations in the liqueur was monitored.

Figures 1a and b show the plot of normalized scale growth for each of the three scale inhibitors as a function of radiation dose, respectively, in the low kilo-rad range and from 0 to 10 mega-rad. The measurement of scale growth relates the amount of NAS solids formed in the inhibited test against that produced from a control test without inhibitor. Below 50 kilo-rad exposure level, these normalized scale growth plots show that both Epsilon and Tau inhibitors almost completely suppressed NAS formation (Fig. 1a). Below 50-kilo-rad exposure of the Omega-doped



(a)



(b)

Figure 1. Scale inhibitor performance as a function of absorbed radiation dose.

samples NAS suppression by Omega was limited to a range of about 60–82% effectiveness. The Omega inhibitor did not fare that well in the suppression of NAS formation, especially above the 50 kilo-rad exposure level for the reaction mixtures. On the other hand, both Epsilon and Tau inhibitors seemed to perform well in suppressing NAS formation past the 1 mega-rad exposure level. The NAS suppression performance for both Epsilon and Tau antiscalants seems to start fading below 80% after about 5 mega-rad exposure. By 10-mega-rad the effectiveness of the Epsilon antiscalant is down to zero, while the Tau antiscalant still shows about 5% effectiveness. However, from the potential application at SRS for this NAS inhibitor technology in a nuclear environment, these data show all three inhibitors would work well. The expected dose the inhibitor would receive is less than 50 kilo-rad. Therefore, all of the inhibitors meet the expectation of preventing scale during the evaporation process.

When examining the data from Figs. 1a and 1b, from the stand point of preventing downstream impact, it appears that the Omega inhibitor decomposes rapidly and the Epsilon and Tau materials survive the radiation. A rapid decomposition allows for the precipitation of aluminosilicate in the drop tank of the evaporator system. Depending on the actinide concentrations in the supernatant liquor, precipitation is favored due to the presence of large amounts of sodium in the form of saltcake. Sodium can be credited as a neutron poison in the event that uranium is co-precipitated with the NAS solids as has been observed historically (10,11). Therefore, from the data as a whole, the inhibitor that performs the best and meets the first two attributes is the inhibitor Omega since there is adequate performance during evaporation and rapide prevention of NAS precipitation.

Additional testing was performed to examine the sensitivity of the inhibitor dosage to the formation of NAS solids. Shown in Fig. 2 is a plot of inhibitor performance as a function of inhibitor dosage at a set radiation dose of 100 kilo-rad. The data in Fig. 2 shows that each of the inhibitors will perform at this radiation dose at an inhibitor dosage of 500 ppm. Decreasing the inhibitor dosage to 100 ppm shows that Epsilon performs while the other two do not. Because of the performance result of the inhibitor Tau in the simulant tests, no testing with the Tau material was pursued further with the exception of tests with actual nuclear waste as shown in Fig. 5.

In addition to monitoring for changes in the amount of NAS minerals formed as a measure of inhibitor performance relative to the reference tests without the inhibitors present in the reaction mixture, a complimentary and confirmatory monitoring for silicon was also obtained. Silicon, which is the principal limiting synthesis reagent in this

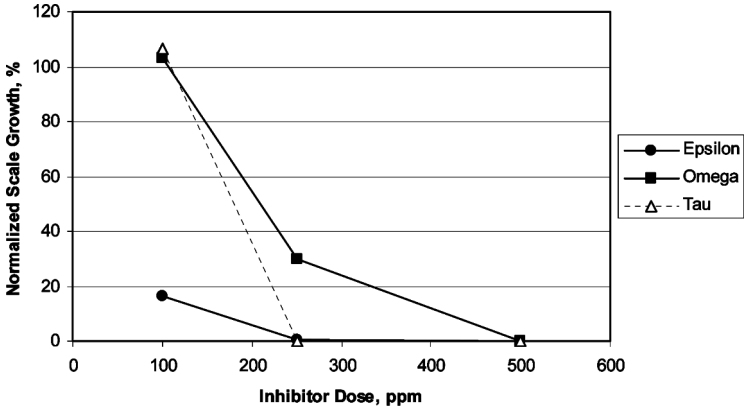


Figure 2. Inhibitor performance as a function of inhibitor dosage at a specific radiation dose.

study, was monitored in the post-synthesis liquor to estimate the extent of NAS formation or suppression. The idea being that after synthesis if there is little or no suppression of NAS formation one would expect that most of the soluble silicon would have reacted to form solids of NAS minerals, which would constitute the bulk of the solid fraction after synthesis. On the other hand, if there is significant suppression of NAS formation, the post-synthesis liquor would contain significant amounts of soluble silicon in solution. On this basis, the quantity of silicon in the post synthesis liquor for the reference samples as well as those for the three antiscalant samples were monitored during this part of the study.

Figure 3 shows a summary plot of the relative percent of silicon left in solution after each test for each of the three polymers at different kilo-rad exposure levels. The reference sample results, as expected (Figure 3), also show that only about 6% of the soluble silicon is left in solution because most of it had gone into the synthesis of NAS minerals.

In Fig. 3, the Epsilon antiscalant spiked samples show the amount of soluble silicon left in solution below the 50 kilo-rad radiation exposure is greater than 80%. Past this 50 kilo-rad level of radiation exposure, the amount of silicon left in solution drops down to about an average of 65% with increase in exposure to radiation. The silicon concentration after this drop seems to stay constant at about 65% for up to 1 mega-rad exposure. After 1 mega-rad exposure, Epsilon-bearing sample performance in suppressing NAS formation drastically drops and by about 2.5 mega-rad exposure, the performance is below 20%.

The Tau antiscalant polymer behavior based on the silicon concentration in the post-synthesis liquor at this kilo-rad exposure levels

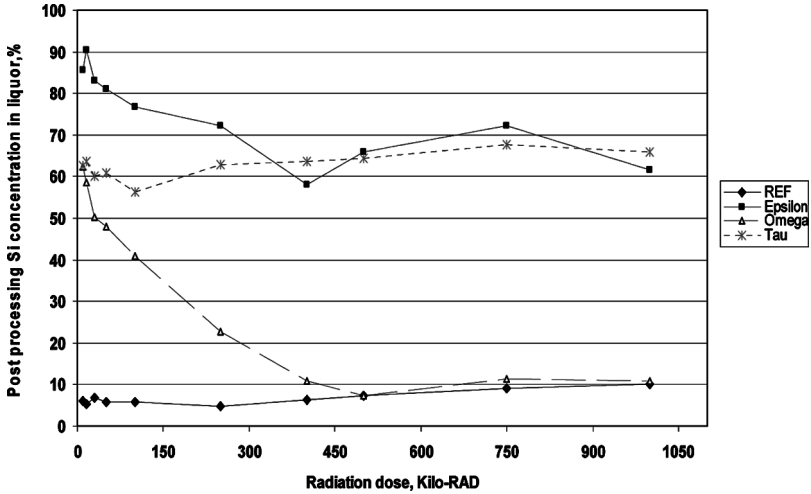


Figure 3. Silicon concentration changes with radiation exposure for epsilon, omega and tau spiked simulants.

(Fig. 3) seems to be fairly consistent. The percent silicon concentration in solution averaged above 60% through out this radiation exposure range. However, at 1.5 mega-rad exposure or there after, there is a steady decrease in the Tau polymer's ability to suppress NAS formation. After 10 mega-rad exposure, its performance is about equal to samples without antiscalant treatment or the reference samples.

The relative percent silicon in the post-synthesis liquor for the Omega antiscalant test samples in the 10 and 15 kilo-rads runs were initially reasonably high at about 60%, however, above the 15 kilo-rad level the amount of soluble silicon in solution dropped exponentially with increase in radiation exposure. By about 400 kilo-rad exposure, the amount of silicon in solution was comparable to that of any reference sample; meaning that the suppression of NAS formation had come to a complete halt (Fig. 3).

Preventing NAS precipitation is not the entire picture. The ideal inhibitor would perform during evaporation, allow NAS precipitation within the evaporator system, and not lead to downstream impacts. Testing was performed to examine the latter impacts via the second set of testing where the inhibitors were irradiated and subjected to analytical characterization with size exclusion chromatography.

Shown in Fig. 4 are the overlay plot results of quantifying the inhibitor concentration as a function of dose for Epsilon and Omega, respectively. The Epsilon post-irradiation exposure concentration decreased

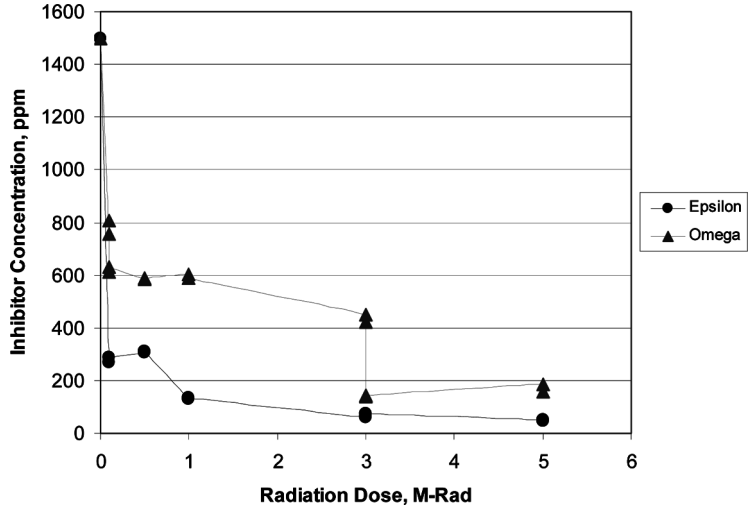


Figure 4. Inhibitor concentration changes as a function of radiation dose.

from an initial 1,500 ppm concentration down to about 50 ppm. However, the largest drop in Epsilon concentration occurred at the lowest radiation exposure levels. For example, in the Epsilon post-irradiation

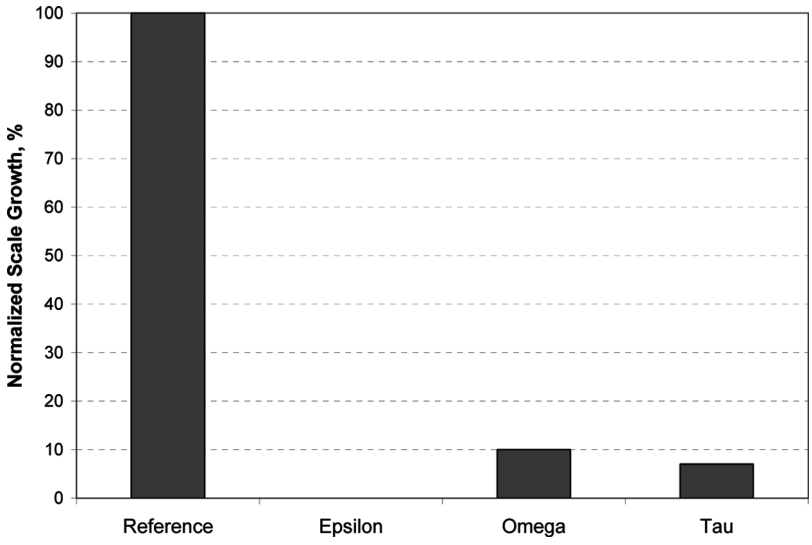


Figure 5. Results of NAS inhibition in an actual waste matrix.

exposure concentration for the 0.1 Mrad irradiated Epsilon bearing sample, the final concentration dropped to about 290 ppm. After that the decrease in polymer concentration with increasing radiation level was found to be gradual. On the other hand, in the Omega based antiscalant samples, the decrease in concentration was less pronounced. The measured concentration after 5 Mrad exposures was found to be about 150 ppm. In this case the drop in antiscalant concentration was initially high. For example, in the 0.1 Mrad irradiation exposures of Omega-bearing simulant samples the Omega concentration dropped down to about 800 ppm from an initial concentration of 1500 ppm. After that the decrease was more gradual.

The Epsilon inhibitor shows the most rapid decomposition. However, both inhibitors decompose rapidly enough to have completely decomposed prior to de-inventorying the waste out of the evaporator system.

In order to ensure that the potential application of the inhibitor technology will perform as expected in actual nuclear waste service, the inhibitors were tested in an actual waste sample that previously had actinides, cesium and strontium removed. Shown in Fig. 5 are the results of testing the three inhibitors for preventing NAS solids formation. The inhibitor loading was 300 ppm in these tests. Due to a limited quantity of actual waste these tests were single runs. Within the expected experimental uncertainty, each of the inhibitors prevented solids formation.

CONCLUSIONS

A successful application of the NAS scale inhibitor technology for nuclear plant operations bring a plethora of constraints that typically would not exist in an industrial setting. In this work, three potential scale inhibitors have been examined as to the radiation stability or perhaps better stated limited radiation stability with regards to preventing aluminosilicate scales in the waste evaporators.

The desired outcome of an inhibitor application would be for the inhibitor to survive radiolytic and chemical degradation long enough for the waste to be evaporated and then decompose rapidly. All three potential inhibitors tested show acceptable performance for preventing NAS solids formation without radiation in simulated wastes and in an actual waste matrix. One inhibitor, Omega, appears to survive the harsh conditions within the evaporator (chemical, radiolytic, and thermal) but decomposes rapidly as a function of the absorbed dose. This benefit has led to the proposed use of the inhibitor Omega at the Savannah River Site. Efforts are currently underway to synthesize industrial scale

quantities of the NAS inhibitor for final testing prior to deployment in an SRS evaporator.

REFERENCES

1. Addai-Mensah, J.; Gerson, A.R.; Zheng, K.; O'Dea, A. (1997) The precipitation Mechanism of Sodium Aluminosilicate in Bayer Plants, *Smart, Light Metals*, 23–28.
2. Gerson, A.R.; Zheng, K. (1997) Transformation, of Sodalite to Cancrinite, *J. Crystal Growth*, *171*: 209–218.
3. Roach, G.I.D.; Cornell, J.B. Scaling in Bayer Plants, (1985) Chemeca 85: Innovation Process Resour. Ind., Aust. Chem. Eng. Conf., 13th, 217–222.
4. Yamada, K.; Yoshihara, M.; Tasaka, S. (1985) Properties of Scale in Bayer Process, *Light Metals*, 223–235.
5. Bickmore, B.R.; Nagy, K.L.; Young, J.S.; Drexler, J.W. (2001) Nitrate-Cancrinite Precipitation on Quartz Sand in Simulated Handford Tank Solutions, *Environ. Sci. Technol.*, *35*: 4481–4486.
6. Ulmgren, P. (1987) The removal of Aluminum form the Recovery System of a Closed Kraft pulp mill, *Nordic Pulp and Paper Res. J.*, *2* (1): 4–9.
7. Park, H., Englezos (1999) Chemical Interactions of UOP IONSiV® IE-911 (CST) with SRS Waste Simulants, *Ind. Eng. Chem Res.*, *38*: 4959–4965.
8. Addai-Mensah, J.; Li, J.; Zbik, M.; Wilmarth, W. (2005) Crystallization and Fouling behavior of Uranium and Sodium Aluminosilicate based Solids in High level—Nuclear Waste Evaporators, Smart Solutioons Doing More with Less, Chemeca 2005, Conference Proceedings, 1–7, Brisbane Queensland, Australia, Chemeca.
9. Wilmarth, W.R.; Rosencrance, S.W.; Hobbs, D.T.; Jantzen, C.M.; Laurinat, J.E.; Van Pelt, W.B.; Tamosaitis, W.L.; Mattus, A.J.; Hu, M.Z.; DePaoli, D.W.; Weber, C.F.; McGinnis, C.P.; Mattigod, S. (2002) Aluminosilicate Formation in High Level Waste Evaporators: A Mechanism for Uranium Accumulation, Proceedings of Waste Management, 2002.
10. Wilmarth, W.R.; Thompson, M.C.; Martino, C.J.; Dukes, V.H.; Mills, J.T.; Boley, C.; Lewis, B.L. (2003) Nitric Acid Cleaning of a Sodalite-Sodium Dilurinate Scale in High Level-Waste Evaporators, *J. of Sep. Sci. and Tech.*, *38*: 3249.
11. Addai-Mensah, J.; Li, J.; Zbik, M.; Wilmarth, W. (2005) Microstructural and uranium Adsorption Behavior of Sodium Aluminosilicate Polytypes in Caustic Aluminate Liquors, *Light Metals*; Minerals, Metals, and Materials Society: p. 171.
12. Addai-Mensah, J.; Li, J.; Zbik, M.; Wilmarth, W.R. (2005) Uranium Sorption on Solid Aliminosilicate Phases under Caustic Conditions, *J. of Sep. Sci. and Tech.*, *40*: 267.
13. Addai-Mensah, J.; Gerson, A.R.; Jones, R.; Zbik, M. (2001) Reduction of Sodium Aluminosilicate Scales in Bayer Plant Heat Exchangers, *Light Metals*, 13–18.

14. Spitzer, D.P.; Rothenberg, A.S.; Heitner, H.I.; Kula, F. (2005) US Patent No 6,814,873, D. Spitzer, A. Rothenberg, H.I. Heitner, F. Kula, M. Lewellyn, Reaagents for the Elimination of Sodalite Scaling, *Light Metals*, 183–188.
15. Walker, D.D.; Norato, M.A.; Campbell, S.G.; Crowder, M.J.; Fink, S.D.; Fondeur, F.F.; Geeting, M.W.; Kessinger, G.F.; Pierce, R.A. (2005) Cesium Removal from Savannah Reiver Site Radioactive Waste using Caustic-Side Solvent Extraction, *J. Sep. Sci. and Tech.*, *40*: 297.