

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Zeolite Characterization

by

William D. Jacobs and Herbert L. Nigg
Savannah River National Laboratory
Aiken, SC 29808

A paper proposed for the
Fall 2007 AIChE Conference
Salt lake City, Utah
November 4 - 9, 2007

and for publication in the proceedings of the meeting

This paper was prepared in connection with work done under Contract No. DE-AC09 96SR18500 with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

Zeolite Characterization AIChE 2007 FALL PROCEEDINGS

Wm. D. Jacobs and Dr Herbert Nigg, Savannah River National Laboratory, Aiken, SC

Abstract

The Savannah River Site isolates tritium from its process streams for eventual recycling. This is done by catalyzing the formation of tritiated water (from process streams) and then sorbing that water on a 3A zeolite (molsieve) bed. The tritium is recovered by regenerating the saturated bed into a Mg-based water cracking unit.

The process described has been in use for about 15 years. Recently chloride stress corrosion cracking (SCC) was noted in the system piping. This has resulted in the need to replace the corroded piping and associated molecular sieve beds.

The source of chlorine has been debated and one possible source is the zeolite itself. Since new materials are being purchased for recently fabricated beds, a more comprehensive analysis protocol for characterizing zeolite has been developed. Tests on archived samples indicate the potential for mobile chloride species to be generated in the zeolite beds.

Discussion

Water forming/absorption as a means of sequestering trace amounts of tritium (a radioactive isotope of hydrogen) has been used at the Savannah River Site for approximately 56 years. But only recently has chloride induced stress-corrosion cracking been observed in the relevant facilities, prompting an investigation of chloride's potential sources.

Savannah River uses hydrogen gas from the process or from the hot Mg bed to act as a carrier gas when regenerating the zeolite beds. A literature search has indicated that this is a unique application for this type of material in gas drying whose potential influence is being investigated. Additionally, recent process changes have introduced the possibility of condensate in corroded lines. This is a definite corrosion promoting phenomena but it still requires a corrosive, i.e., chlorides.

The process has a strict 250 ppm limit for total chloride content for any materials which come in contact with stainless steel and historic quality assurance testing showed this to be true for zeolite. However, such testing was done by colorimetric spectrophotometry of DI water used to 24 hr soak zeolite samples. these values were typically 10 ppm.

Since it had been almost 15 years since the last procurement of Type 3A zeolite, a search for qualified vendors was begun based on a new testing protocol. The Site has historically used two popular vendors over the last forty years and has some quality assurance test results for those samples. Some of those materials were also archived. Both vendors are participating in the current material procurement.

Various characterization tests have been proposed to determine the potential for chloride, other species and particulate to be generated from historic and newly acquired materials. These include TGA, cold and hot leach sent to ion chromatography, KOH digested samples sent to ion chromatography, XRF, XRD, sieve-testing and NAA. The purpose of these tests is to look for chloride (leachable), chloride (bound or total), fluorides, sulfides and phosphates and particulate formation. The results vary substantially for the two vendors who supplied new materials. For example, chloride (total) may vary from 200 ppm to 3000 ppm.

Other methods for characterizing the Type 3A zeolites include X-Ray Diffraction

(XRD) and X-Ray Fluorescence (XRF) to study the composition, the nature of the chlorides, and the structure of the zeolite samples. The XRF analysis was determined to be of little analytical value for chloride analysis since the technique is not used for elements with a mass less than 23. However, the XRD did show significant differences in the two historic vendor's materials. The XRD analysis yielded information that indicated that similar materials, both branded Type 3A, are significantly different in composition. But the data could not indicate the nature of the chlorides in the zeolite structure.

Conclusions

Testing continues on the vendor samples. The results of all the tests are summarized in the presentation. Additional efforts include actual testing of water sorption capacity and the influence of common contaminant gases on water sorption capacity. Tests that expose new and archived samples to radiation are being developed in an attempt to determine if radiolysis can produce mobile, corrosive species.