Considerations for using Marinite in Refined GSI-191 Chemical Effects Testing

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Considerations for using Marinite in Chemical Effects (CE) Testing

Background

Marinite is used in the Calvert Cliffs Nuclear Power Plant (CCNPP) containment as a fire barrier on cable trays. Marinite is a generic term of a mixture of calcium silicate, calcium metasilicate (wollastonite), and re-enforcing fibers (fiberglass, organic fibers such as cotton). The Marinite at CCNPP is made by BNZ Materials and comes in a variety of forms ranging from molded casts, boards, and flour. BNZ Materials Marinite I or M are the types of Marinite found in the CCNPP containment (Ref. 1, Attachment 13). BNZ Materials Marinite I or M boards have a nominal density of 46 lbs/cuft (Ref. 1, Att. 13, Page 6 of 13) and are promoted as having high strength and damage resistance.

Marinite debris historically has been modeled as $10 \, \mu m$ particulate spheres for hydraulic characteristics in debris bed head loss testing. The use of Marinite particulate in chemical effects testing is problematic as the Marinite particles are difficult to contain and tend to transport to the debris bed which increases debris bed differential pressure through mechanical influences thereby masking increases in debris bed differential pressure caused by chemical effects.

Approach

Marinite particles produced during mechanical manufacturing processes (assumed pretty well formed spherical particles) as measured by BNZ Materials range from roughly 44 μ m spheres to 250 plus μ m spheres with 96% of the particles being larger than 44 μ m in diameter (Ref. 3). Therefore determining the surface area based on claiming ALL are 44 μ m spheres is conservative.

Marinite board of the appropriate total surface area equal to the 44 μ m spheres is to be used in chemical effects tests. The boards have surface roughness, evaluated that to be about Ra = 6.3 μ m. The surface roughness appeared to be mostly ridges like isosceles triangles that covered the surface. Therefore, the ridged surface area is computed per unit area of the Marinite board and found to be 2.3x that of the flat board. Assuming 2.0x was slightly conservative and bounding. (i.e., 401.6 square meters of 44 μ m spheres would need 401.6 square meters of board [areas of top, bottom, and edges included] divided by the surface roughness effect of 2.0 results in 200.8 square meters of board). So now the amount of Marinite board exposed surface equal to the 44 μ m spheres appropriate for the chemical effects tests is known.

Lastly, use of that area of board would put more mass of Marinite into the test that the same area of 44 μ m spheres. That mass would be available to dissolve in the test; not that it will dissolve, just that it is present and could dissolve. As the surface dissolves away, more board is exposed. If the processes can dissolve all of the 44 μ m spheres, it might be able to dissolve much of the board (and more mass than is available in the spheres). Potentially, the use of board could be significantly over-conservative.

Recommended Surrogate for Marinite

The following are the responses and recommended surrogate for chemical effects testing of Marinite following a hypothetical LOCA:

Outside a HELB ZOI:

Marinite outside a HELB ZOI will not be source of debris fines. Marinite outside a HELB ZOI may be either exposed to sprays or submerged. Marinite in service at CCNPP is ½" thick (Ref. 1, Att. 10, Page 5 of 8). Therefore, ½" thick pieces of BNZ Material Marinite I or M board are appropriate for CCNPP Chemical Effects tests.

Inside a HELB ZOI:

Marinite debris from a HELB ZOI will be small pieces (0.5%), large pieces (2.7%) and 95.5% will remain intact on the cable tray as intact pieces (Ref. 2, Table 3c1-2, "Marinite Size Distribution", page 97). 1.3% of the Marinite inside a HELB ZOI is assumed to fail as fines (particulate) (Ref. 2, same table as above).

Marinite Small Pieces, Large Pieces, and Intact Pieces

• ½" thick pieces of Marinite I or M boards can be used as a surrogate for Marinite small pieces, large pieces, and intact pieces.

Marinite Fines:

- Marinite fines can be used in Chemical Effects testing where the transport of particulate is not
 an issue, e.g. beaker bench top tests. Marinite particulate can be purchased from BNZ Materials
 as Marinite Fines, a manufacturing byproduct from sanding and cutting of Marinite I and M
 boards. Marinite Fines is an appropriate surrogate for Marinite particulate from a HELB ZOI since
 the break-up by sanding and cutting would be analogous to the break-up of the Marinite board
 within the ZOI. Attached is the BNZ Materials analysis of Marinite Fines (Ref 3).
- $\frac{1}{2}$ " thick pieces of Marinite I or M boards can be used as a surrogate for Marinite fines where the transport of particulate is problematic. The surface area of the Marinite board will be calculated assuming the Marinite particulate to be 44 μ m in diameter as discussed above and presented below.

Surface Area of Marinite Board to Represent Fines in Chemical Effects Testing

Reference 1 determined that 0.104 cubic feet (Ref. 1, Page 14, Section 8.0) of Marinite board would become particulate debris in a design basis LOCA at CCNPP. Using the above evaluation of 44 μ m diameter, this volume of Marinite particulate would produce an exposed surface area of 4,323 square feet. Such scaling ignores the surface contours and roughness of the Marinite board.

Computation of Particulate Parameters:

- 1. 0.104 cubic feet = 0.002945 cubic meters
- 2. Sphere volume
 - a. $44 \mu m diameter = 4/3\pi r^3 = 4/3\pi (44x10^{-6} m/2)^3 = 44.60x10^{-15} m^3 per particle$
- 3. Number of spheres that equals the above volume of Marinite blasted
 - a. Number of 44 μ m diameter spheres = Volume/Volume of one sphere= $2.945 \times 10^{-3} \text{m}^3 / 44.60 \times 10^{-15} \text{m}^3 \text{per sphere} = 66.03 \times 10^9 \text{ spheres}$
- 4. Sphere surface area
 - a. $44 \mu m \text{ diameter} = 4\pi r^2 = 4\pi (44 \times 10^{-6} \text{ m/2})^2 = 6.082 \times 10^{-9} \text{ m}^2 \text{ per particle}$
- 5. Total Surface Area of Spheres
 - a. $44 \mu m \text{ diameter} = \text{Number of spheres x sphere surface area} = 66.03 \times 10^9 \text{spheres x } 6.082 \times 10^{-9} \text{m}^2 \text{ per sphere} = 401.6 \text{ m}^2$

Recent evaluation of a sample of Marinite board from CCNPP determined the surface roughness to be R_a =6.3 μ m. See Figure 2 for a photograph of a small piece of Marinite, approximately 1 inch long. Assuming each surface feature is a 'ridge' 6.3 μ m tall with base of 6.3 micrometers and the surface is completely covered by such features would yield an exposed surface of 2.23 times the apparent board surface assuming a perfectly smooth surface. Therefore, scaling particulate to surface area without considering surface roughness results in a greater than a 2 times over estimate of required surface area.



Figure 2: Marinite Board, ~3 centimeters long, Surface Roughness R_a=6.3 μm

Computation of Bulk Marinite Surface Area Parameters:

- 1. Area of Ridge (assumed to be isosceles triangle in cross section):
 - a. 6.3 µm tall with 6.3 µm base x length of the sample = $2 \times L \times \sqrt{(3.15 \ \mu m)^2 + (6.3 \ \mu m)^2}$ = $2 \times L \times 7.044$ µm per ridge
- 2. Number of ridges = width $/ 6.3 \mu m = W/6.3 \mu m$
- 3. Total Ridge Area = $W/6.3 \mu m x (2 x L x 7.044 \mu m per ridge) = W x L x 2.236$

Therefore, the ridges increase the surface area by more than a factor of 2.3x.

Furthermore, use of a half inch thick board adds much more mass to the test, allowing any dissolution to proceed to far greater extent than could dissolution of 44 μ m particles (not faster but to a potentially greater mass dissolved).

Conclusion

Marinite board used as a surrogate for Marinite particulate will have total surface area 50% of the total surface area of the number of 44 μ m spherical particles calculated to be produced for each break (50% is based on the surface roughness computation above). For the example presented above, the surface area to be used in a chemical effects test would be 0.50 x 401.6 m² = 200.8 m² scaled to the volume of the test fluid.

References

- 1) CCNPP Calculation CA06940 Rev. 0001, "Computation of Aluminum and Marinite Board Debris Loads", March 23, 2009.
- 2) Attachment 3 to AEPNRC: 8054-02, NRC Accession Number ML080770395.
- 3) Fax from Norman R. Scheffer, Product Development, BNZ Materials, to Gilbert Zigler, ENERCON, dated 09/13/2013 (Attached).

Attachment

Fax from Norman R. Scheffer, Product Development, BNZ Materials, to Gilbert Zigler, ENERCON, dated 09/13/2013

MARINITE^R FINES SELECTED CHEMICAL AND PHYSICAL CHARACTERISTICS

* Chemical Composition:

Substance	Typical Analysi: % Dry Weight
Calcium Metasilicate (Wollastonite) (CaO SiO ₂)	48.0
Calcium Silicate (5CaO 6SiO, 2.5H,O)	37.0
Calcite (CaCO ₃)	7.0
Organics (Cellulose Fibers)	4.0-6.0
Chopped Glass	0.0-6.0
Crystalline Silica Quartz	0.0-0.7

- * pH (5% slurry by weight): 10.9
- * Density: 24.5 Lb./CuFt.
- * Specific Gravity: .4 LBD, 40-65 PBD
- * Melting Point: >1900 Degrees F
- * Screen Analysis:

	Sambre
Tyler Screen	Cumulative & Retained
35 mesh	1
65	3
80	5
100	26
200	56
325	96

- * Color: Light goof BEIGE OFF WHITE
- * Quantity: Up to 75,000 pounds per month, subject to availability
- * Possible Applications:

Absorbents	Fireproofing	Plastics
Cements	Insulating powders	Soil amendments
Ceramics	Neutralizing agents	Reinforcing agents
Coatings	Paints	

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